1-1-2013

Early Transition Metal CCC-NHC Pincer Complexes: Synthesis, Characterization, and Catalysis

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EARLY TRANSITION METAL CCC-NHC PINCER COMPLEXES: SYNTHESIS, CHARACTERIZATION, AND CATALYSIS

A Dissertation
presented in partial fulfillment
of the requirements for the degree
Doctor of Philosophy
in the
Department of Chemistry and Biochemistry
The University of Mississippi

by

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ADVISOR: PROFESSOR T. KEITH HOLLIS

December 2013

ABSTRACT

The previously reported amine elimination methodology for the metalation of CCC-NHC pincer ligand precursors has been extended to other early-transition metals and ligands. Specifically, synthetic results for the preparation of imidazole based CCC-NHC pincer Ti (IV), CCC-NHC pincer Ta (V) will be discussed. In addition, the synthesis of a new triazole based CCC-NHC pincer ligand precursor and its metalation with Ta (V) will be presented. Coordination sphere manipulation of the new pincer complexes using TMSCl for the Ti complex and lithium t-butylamide for the Ta complexes is also discussed. The reaction of the initial Ta CCC-NHC complex with lithium t-butylamide is of particular interest as it is the first X-ray crystallographically determined molecular structure of an early-transtion metal anionic N-heterocyclic carbine complex. Catalytic results in hydroamination/cyclization with the Ti complexes and oxidative amination using the Ta complexes will also be reported.

LIST OF ABBERVIATIONS AND SYMBOLS

NHC	N-Heterocyclic Carbene
MIC	Mesoionic Carbene
NHDC	Anionic N-Heterocyclic Dicarbene
CCC	Carbon, Carbon, Carbon (denotes which atoms of the pincer ligand are bonded to the metal)
Ta	Tantalum
Ti	Titanium
Zr	Zirconium
NMR	Nuclear Magnetic Resonance
Bu	Butyl
t-Bu	tert-butyl
EA	Elemental Analysis
δ	Chemical Shift (ppm, NMR)
J	Couppling Constant (Hz, NMR)
TMSCl	Trimethylsilyl chloride
$Ti(NMe_2)_4$	Tetrakis(dimethylamino)titanium(IV)
$Zr(NMe_2)_4$	Tetrakis(dimethylamino)zirconium(IV)
$t\text{-}BuN{=}Ta(NMe_2)_3$	t-butylimidotris(dimethylamido)tantalum(V)
Tol	Toluene

Et_2O	Diethyl Ether
CH_2Cl_2	Methylene Chloride
DMSO	Dimethyl Sulfoxide
CD_2Cl_2	Deuterated Methylene Chloride
C_6D_6	Deuterated Benzene

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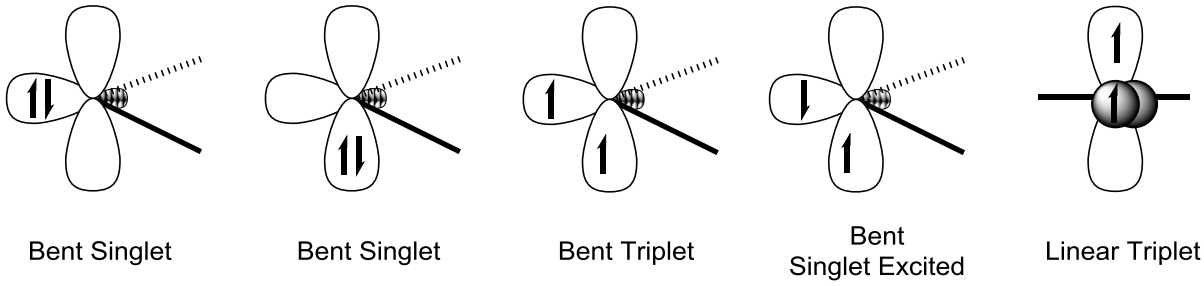
CHAPTER 1

INTRODUCTION TO CCC-NHC PINCER LIGANDS

1.1 Carbenes

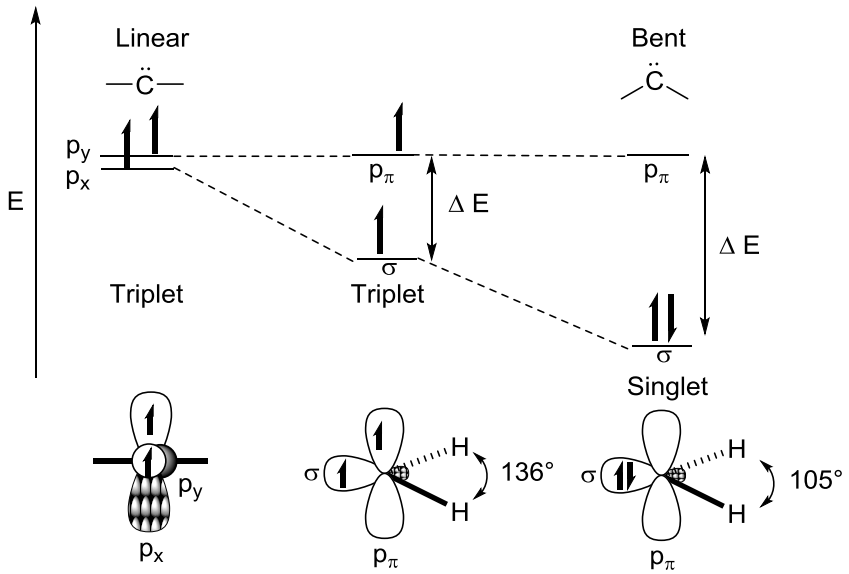
Carbenes are defined as reactive, uncharged, divalent carbon species with six electrons in their valence shell.[1] The seminal work on carbene was first published by Buchner over a century ago.[2,3] Carbenes can have either a singlet or triplet spin state and adopt a linear or bent geometry (Figure 1.1.1). The spin state of a carbene is determined by the difference in energy between promoting one of the electrons of the non-bonding pair to a higher energy orbital and the energy required to pair both non-bonding electrons in the same orbital. For example, linear carbenes are triplet carbenes. Linear carbenes have an sp hybridization and two non-bonding degenerate orbitals (p_x and p_y). Consequently, the energy to promote one of the non-bonding electrons from the p_x orbital to the p_y orbital is less than the energy needed to pair both electrons p_x orbital **(**Figure 1.1.2). Thus, the non-bonding electrons occupy different orbitals with the same spin, yielding a triplet carbene.

Figure 1.1.1 Possible Geometries and Spin States of Carbenes.



The degeneracy of the frontier orbitals in carbenes is broken in the more common bent geometry. In a bent geometry the hybridization of the carbene carbon is sp^2. The p_y orbital remains essentially unchanged and is designated as the p_π orbital in a bent carbene. The formally pure p_x orbital in the linear carbene is stabilized from the s character it acquires in the bent geometry and is now designated the σ orbital. Depending on how stabilized the σ orbital is on the spin state of a bent carbene may be triplet or singlet. In the example of a bent carbene with an H-C-H bond angle of 136°,[4] the σ orbital is not stabilized enough for the energy gap between the σ and p_π orbitals to be greater than the energy to pair both electrons in the same orbital. Thus both non-bonding electrons occupy different orbitals, adopt parallel spins yielding a triplet carbene (Figure 1.1.2). Conversely, in the example of a bent carbene where the H-C-H bond angle is 105°,[4] the σ orbital is stabilized enough for the energy gap between the σ and p_π orbitals to be greater than the energy to pair both electrons in the same orbital and the frontier orbitals are designated as p_π and σ. Accordingly, the non-bonding electrons will both occupy the σ orbital with opposite spins, yielding a singlet carbene (Figure 1.1.2).

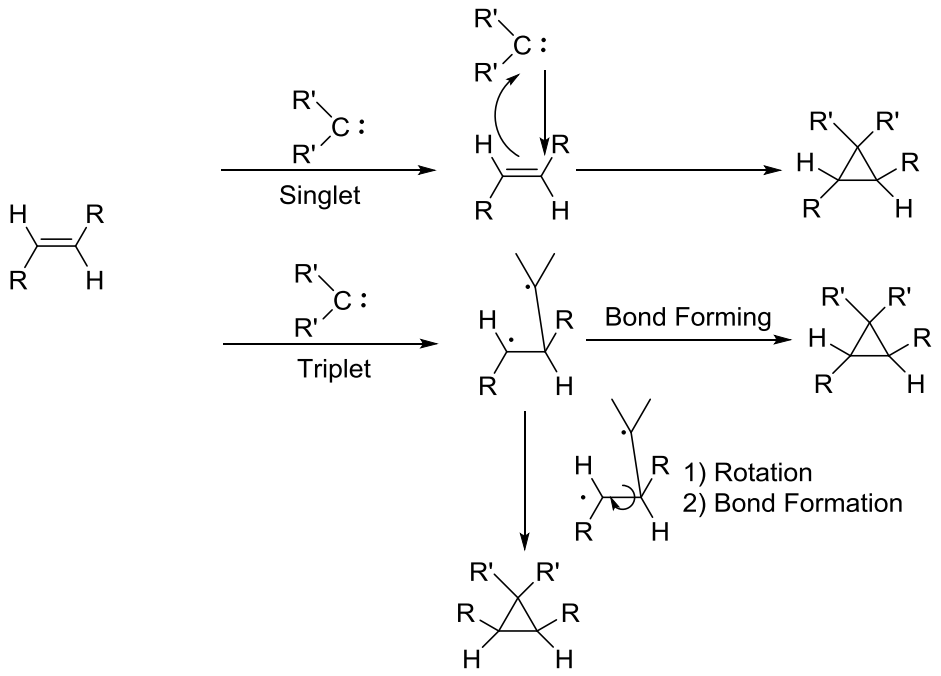
Figure 1.1.2 Singlet vs. Triplet Carbenes.



Pairing energy > ΔE, triplet carbene
Pairing energy < ΔE, singlet carbene

The spin state of carbenes is important, as it affects the reactivity of the carbene. The reaction of carbenes with alkenes to form cyclopropanes is well known and demonstrates how the spin state effects reactivity of the carbene.[1] Singlet carbenes react in a concerted manner with alkenes to form only one stereospecific product. Triplet carbenes react via a diradical type mechanism, where one of the non-bonding electron reacts with the one of the electrons of the π bond. This breaks the π bond and allows former double bond to rotate, prior to reacting with the second electron of the carbene, yielding diaesteromeric products **(**Scheme 1.1.1).[4] From here only singlet carbenes will be discussed in the work, as the N-Heterocyclic carbenes (NHCs) are singlet carbenes.

Scheme 1.1.1 Reaction of Carbene with Alkenes.

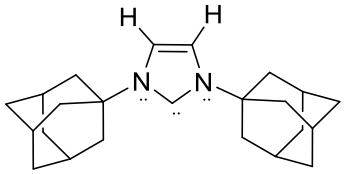


1.2 N-Heterocyclic Carbenes (NHCs) and N-Heterocyclic Carbene Variants

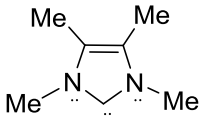
N-Heterocyclic carbene (NHC) complexes were first synthesized by Öfele and Wanzlik in the 1960s.[5,6] Although the first free carbene was reported in 1988 by Bertrand,[7] it was not until 1991 that Arduengo published the first crystal structure of a free carbene.[8] The crystal structure published by Arduengo was that of an NHC. The stability of NHCs was first attributed to the bulky adamantly group bonded to the nitrogens of the NHC. However, following the publication of a methyl substituted NHC X-ray crystal structure in 1992, it was accepted that the electronic configuration of the NHC is the cause of its stability.[9] The non-bonding electrons in the σ orbital of the carbene carbon are stabilized by the electron withdrawing effect of the adjacent nitrogen atoms (Figure 1.2.2). The empty p_{π} orbital is stabilized by the lone pairs on the

adjacent nitrogen atoms, which can delocalize into the empty orbital (Figure 1.2.2). Consequently, NHCs are more stable than other carbene species.

Figure 1.2.1 First Carbenes by Arduengo.

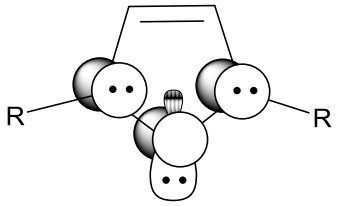


J. Am. Chem Soc. 1991

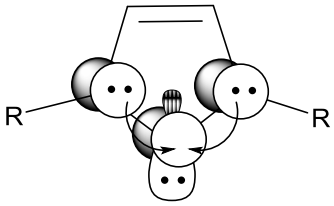


J. Am. Chem Soc. 1992

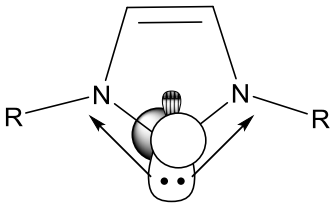
Figure 1.2.2 Electronic structure of NHCs, Nitrogen Lone Pair Donation, and Electron withdrawing Effect.



Electronic Structure of NHC



Lone Pair Donation to p_π Orbital



Electron Withdrawing Effect by Nitrogen Atoms

Because of their strong σ-donating ability, lack of dissociation, and neutral charge, NHCs are considered phosphine complements.[10,11] NHCs have become ubiquitous in late-transition metal complexes and catalysis.[12] They have been successfully applied to a large range of catalytic reactions such as olefin metathesis,[13] C-C coupling,[14] and hydrosilylation.[15] In contrast, early-transition metal NHC complexes, particularly in their highest oxidation state,[12] have yet to be studied in the same depth.[16-39] Group 5 NHC metal complexes are particularly scarce. Fryzuk has reported four, and to date the only, crystal structures of Ta complexes bearing an NHC

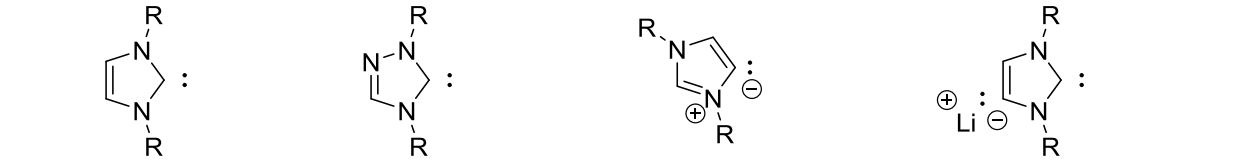
ligand. Reports of Ta NHC chemistry remain sparse despite significant reactivity with Ta which includes N_2 activation,[40-48] CO_2 activation,[49-51] chiral hydroaminoalkylation,[52] and C-N bond activation.[53,54]

Although imidazole-based NHCs constitute the majority of NHC research, new NHC variants have also been synthesized. Noteworthy NHC variants are triazole-based NHCs, C-4 or C-5 bound "abnormal carbenes," and anionic N-heterocyclic dicarbenes (NHDC). Triazole-based NHCs are similar to imidazole-based NHCs; however a methine group is replaced in the cyclic structure with a nitrogen. Depending on the location of the nitrogen in the cyclic structure a 1,2,3,-triazole-based or a 1,2,4-triazole-based complex can be synthesized. In this work we will discuss the 1,2,4-triazole-based NHCs. Triazole-based NHCs are less σ-donating than the imidazole-based NHC due to the electron withdrawing effect of the extra nitrogen. Research into late-transition-metal triazole-based-NHC has been established,[55-63] yet no early-transition-metal (group 3, 4, or 5) triazole-based-NHC complexes have been reported.

Imidazole-based-NHCs bound by the C-4 or C-5 carbon are known as "abnormal carbenes" or Mesoionoic Carbenes (MICs). The term mesoionic carbene is used to describe an NHC ring system where one must assign formal positive and negative charges. No resonance structure with all neutral formal charges can be written in a mesoionic carbene. The first report of abnormal binding to an NHC was in 2001 by Crabtree.[64] It was only just recently that the crystal structure of the first free abnormal carbene was reported by Bertrand.[65] Abnormal Carbenes/MICs are more electron donating than C-2 bound NHCs since they lack a second adjacent electron withdrawing nitrogen.[66] Research into late-transition-metal MICs have been established,[67] yet no reports of early-transition-metal MICs have been reported. In 2010,

Robinson published the first crystal structure of a free anionic N-heterocyclic dicarbene (NHDC) and has subsequently published the Zn complexes bearing the NHDC ligand.[68,69] No X-ray crystal structures of early-transition-metal NHDC have been published to date.

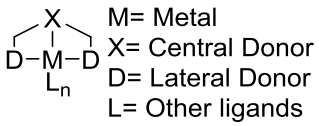
Figure 1.2.3 NHC and NHC Variants.



1.3 Pincer Ligands

The pincer ligand architecture is an important class of tridentate, meridional binding ligands that form robust metal complexes.[70-72] Shaw first synthesized pincer complexes in the 1970s.[73-76] Pincer ligands have application in a variety of reactions;[77-80] noteworthy examples include C-F bond activation,[81,82] alkane dehydrogenation,[72] and catalytic C-C bond formation.[71] The general architecture of a pincer ligand is a central, often aromatic, donor group flanked by two lateral donor groups (Figure 1.3.1). One of the reasons for the widespread use of pincer ligands is the ability to vary the lateral donor groups, providing an effective way to alter the properties of the metal center. Accordingly, incorporation of NHCs into pincer ligands has become of increasing interest.[71,83-88]

Figure 1.3.1 General Structure of a Pincer Complex.

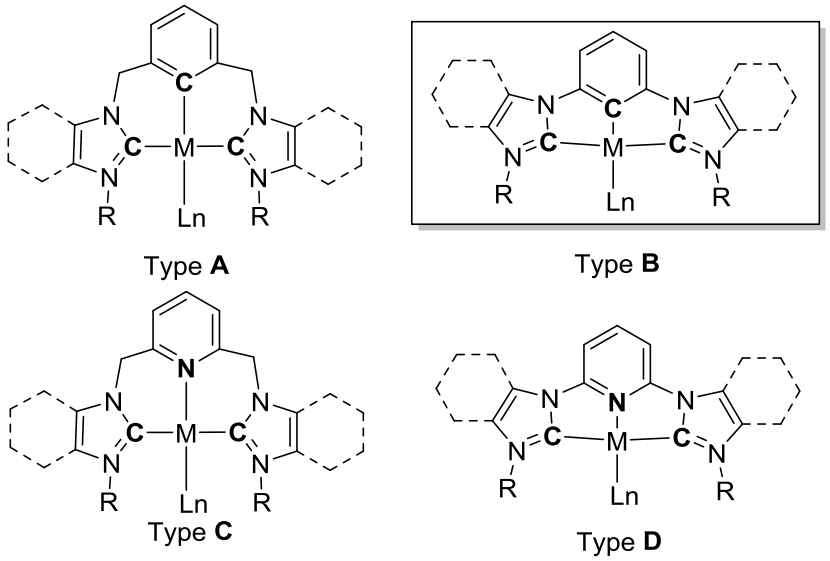


1.4 CCC-NHC Pincer Ligands

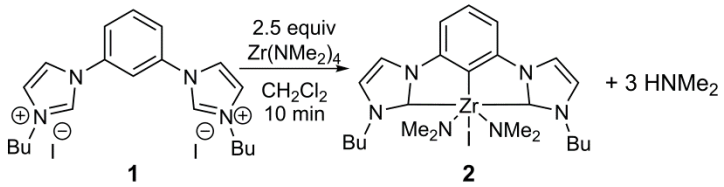
The incorporation of NHCs in a pincer ligand architecture is has become of increasing interest for many groups worldwide.[71,83] Four major classes of bis(NHC) pincer ligands have be studied and are distinguished by two characteristics. The first characteristic is the central aryl donor group being a nitrogen or carbon. The second characteristic is whether there is a methylene spacer in-between between the aryl and NHC donor ligands. The Hollis group has pioneered work involving of Type B bis(NHC) pincer ligands (Figure 1.4.1),[30] and several groups globally have continued developing this class of ligand.[31,32,83,89-99] Use of early-transition metal amido starting materials for triple C-H bond activation of the ligand precursors, via amine elimination, is an effective route to synthesize complexes bearing multidentate ligands.[21,35,36,48,100-106] In particular, this methodology has yielded a facile route for the synthesis of group 4 CCC-NHC pincer complexes. The electrophilicity of the d^0 metal center, in conjunction with the basicity of the dimethylamido ligands, were exploited to facilitate the necessary triple C-H bond activation of the imidazolium salt precursor. An additional advantage that the amine elimination pathway has, in the synthesis of CCC-NHC group 4 pincer complexes, is the ability to vary the non pincer ligands by the amount of metal amido starting material used. It was discovered that use of excess $Zr(NMe_2)_4$ yielded CCC-NHC bis(dimethylamido)iodo Zr complex (Scheme 1.4.1). Using freshly sublimed $Zr(NMe_2)_4$ in a stoichiometric amount with the CCC-NHC ligand precursor in toluene at 160 °C yielded CCC-NHC (dimethylamido)bis(iodo) Zr complex **(**Scheme 1.4.2). This methodology has also been expanded to synthesize the analgous Hf pincer complexes as well **(**Scheme 1.4.2).[32] These group 4 transition metal pincer NHC complexes were shown to catalyze the hydroamination/cyclization of unactivated alkene-

amines(Scheme 1.4.3),[31,32] and to undergo transmetallation to late metal centers (Scheme 1.4.4).[30-32,107]

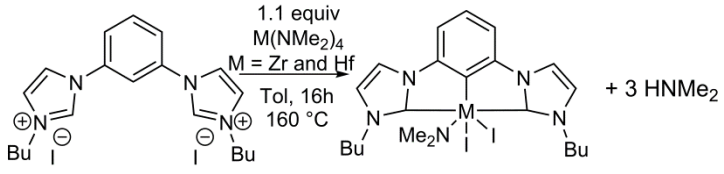
Figure 1.4.1 . Metal Complexes Derived from CCC-NHC Pincer Ligands.



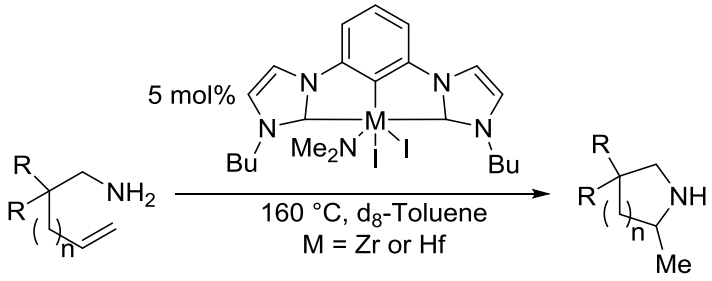
Scheme 1.4.1 Triple C-H Bond Activation of CCC-NHC Ligand Precusor.



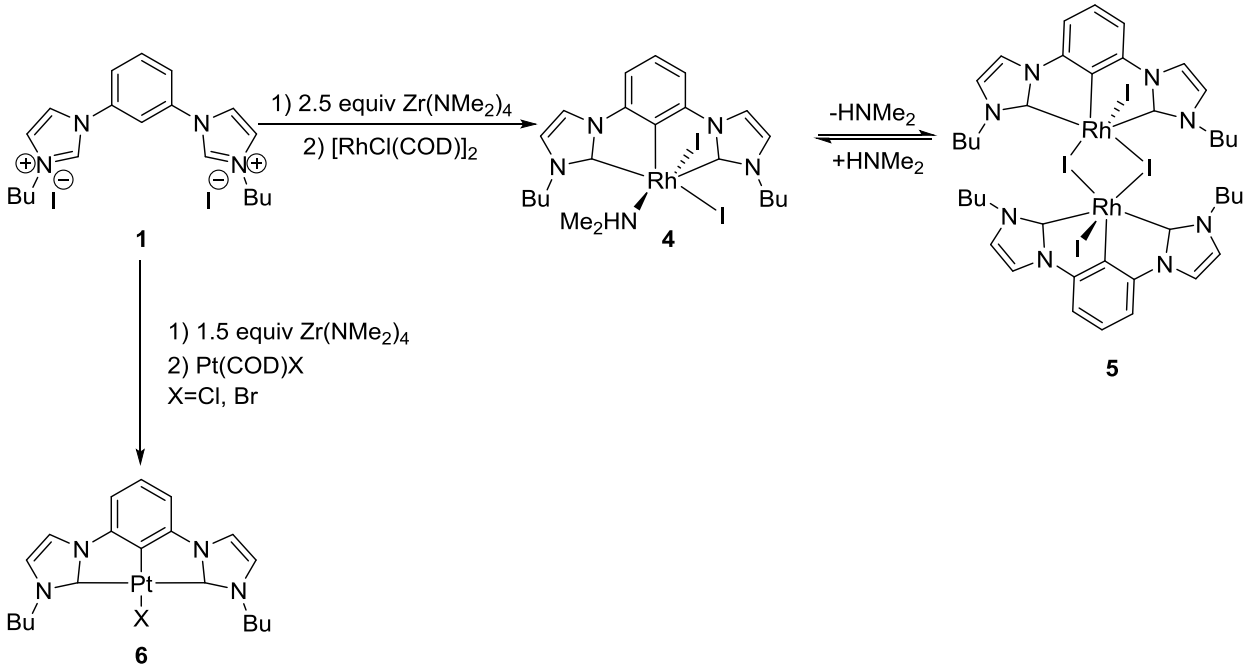
Scheme 1.4.2 Stoichiometric Synthesis of CCC-NHC Group 4 Metal Complexes.



Scheme 1.4.3 Catalytic Hydroamination/Cyclization of Unactivated Alkene-Amines.



Scheme 1.4.4 Transmetallation to Late-Transition Metal Complexes.



The work herein focuses on the extension of the amine elimination methodology to synthesize new early-transition-metal CCC-NHC pincer complexes. Specifically, new Ti and Ta CCC-NHC pincer complexes were synthesized and characterized. Use of $Ti(NMe_2)_4$ as a metalating reagent for the imidazolium salt ligand precursors yielded CCC-NHC pincer Ti dimethylamido halide complexes in good yields. The CCC-NHC pincer Ti bis(dimethylamido)

halide complexes were found to be good catalysts for the hydroamination/cyclization of alkene-amines. Manipulation of the coordination sphere of the CCC-NHC pincer Ti dimethylamine halide complexes was achieved with TMSCl to yield the appropriate CCC-NHC pincer Ti tris(halide) complex. CCC-NHC pincer Ta (*t*-butylimido)(dimethylamido)(iodo) complexes using imidazolyl and triazolyl based ligands were synthesized with Ta(=N*t*Bu$(NMe_2)_3$ as a metalation reagent. The triazole Ta complex is of particular importance as it is, to the best of our knowledge, the first report of an early-transition-metal (group 3, 4, and 5) triazole based NHC complex. Treatment of the CCC-NHC pincer Ta (*t*-butylimido)(dimethylamido)(iodo) with lithium *t*-butylamide synthesized the CCC-NHC pincer Ta bis(*t*-butylimido) complex, which was found to be a great catalyst for oxidative amination/cyclization of alkenyl amines. This reaction is rare as there are only a few reports of the transformation of unactivated amino-alkenes to cyclic imines.[108,109] Upon heating the reaction, during the synthesis of the Ta CCC-NHC pincer bis(*t*-butylimido) complex, a NHDC carbene was formed. The NHDC ligand was bonded to Ta via the C-4 carbon and is the first example of an early-transition-metal MIC and NHDC.

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CHAPTER 2

SYNTHESIS OF TITANIUM CCC-NHC PINCER COMPLEXES AND CATALYTIC HYDROAMINATION OF UNACTIVATED ALKENES

2.1 Research Background

Since the discovery of isolable push-pull and N-heterocyclic carbenes,[1,2] stable carbenes have been the focus of intense research.[3] Because of their strong σ-donating ability and lack of dissociation, they are considered phosphine complements.[4,5] N-heterocyclic carbenes (NHCs), in particular, have become ubiquitous in late-transition metal complexes and catalysis.[6] They have been successfully applied to a large range of catalytic reactions such as olefin metathesis,[7] C-C coupling,[8] and hydrosilylation.[9] In contrast, early-transition metal NHC complexes, particularly in their highest oxidation state,[6] have yet to be studied in the same depth.[10-33] Only a small number of Ti NHC complexes have been reported.[14,16,18,20,27,28,31,32,34-38] Successful applications

of Ti NHC complexes were as efficient catalysts for ethylene and *rac*-lactide polymerization.[20,27,31,34,38]

Pincer ligands are another important class that has been studied extensively.[39] Pincer ligands have been known since the 1970's and have been used to efficiently catalyze a variety of reactions.[40,41] The development of pincer Ir complexes for efficient, catalytic alkane dehydrogenation highlights the importance of pincer ligands in organometallic chemistry.[42] The meridional, tridentate nature of pincer ligands makes them a favored motif for ligand design as the resulting complexes have been demonstrated to be robust.[39] Many research groups have applied stability through chelation in the design of bidentate and tridentate NHC ligands featuring anionic tethers, typically aryloxide or amido functionalities, to overcome the tendency of ligand dissociation from the hard Lewis acidic metal center.[15,23,29,43] Incorporation of NHCs into pincer ligands has become of increasing interest.[40,44,45] Yet, only a few examples of early-transition metal pincer NHC complexes have been reported.[23,46,47]

The Hollis group has previously reported Zr and Hf complexes of a pincer ligand architecture with an anionic phenyl group tethering two NHC groups.[24-26] By exploiting two characteristics of the early-transtion metal amido starting material, the electrophilicity of the d^0 metal center and the basicity of the dimethylamido ligands, the desired triple C-H bond activation of the imidazolium salt precursor was achieved. These group 4 transition metal pincer NHC complexes were shown to catalyze hydroamination/cyclization of unactivated alkene-amines,[25,26] and to undergo transmetallation to late metal centers.[24-26,48] We report, herein, an extension of this methodology to the synthesis and characterization of Ti analogues and their catalytic activity in the hydroamination/cyclization of unactivated alkene-amines.

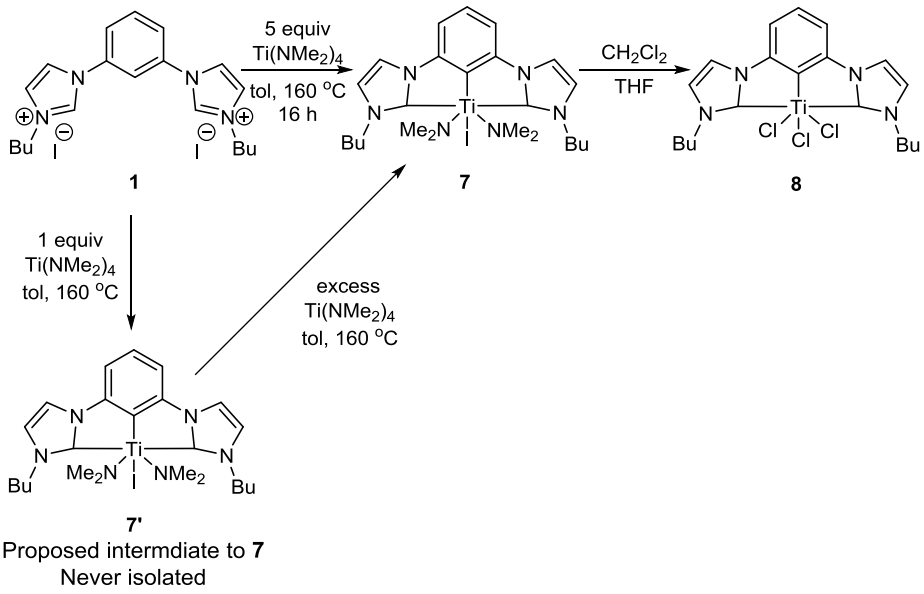
2.2 Results and Discussion

2.2.1 Synthesis and Characterization of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV), (7), and 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV), (8).

Similar to the previously reported procedures for the Zr analogue,[24] bis(imidazolium) diiodide salt **1** was treated with an excess of $Ti(NMe_2)_4$ in toluene at 160 °C for 16 h yielding complex **7** (Scheme 2.2.1.1). The excess $Ti(NMe_2)_4$ was used to ensure that the initially produced (dimethylamido)diiodoTi complex was converted to the desired bis(dimethylamido)(iodo)Ti complex **7**. The most obvious change from the ^{1}H NMR spectrum of bis(imidazolium) diiodide salt **1** after treatment with $Ti(NMe_2)_4$ was the loss of the imidazolium proton signal at δ 11.27. Additionally, the signal corresponding to the butyl methylene group α to the nitrogen shifted from a triplet at δ 4.46 in salt **1** to a triplet at δ 3.93 in complex **7**.[24] As noted for the previously reported Zr analogue,[24] the triplet was consistent with either a symmetric complex with trans amido groups or rapid interconversion within the cis amido coordination sphere. Rapid interconverstion of a complex with cis amido coordination sphere would make the protons on the methylene group adjacent to the nitrogen magnetically equivalent, yielding the observed triplet. This data was consistent with data of the Zr complex, where the X-ray crystal structure contained cis amido groups, yet the NMR data showed a triplet. The carbene peak at δ 190.5 in the ^{13}C NMR spectrum also indicated successful metallation of the salt. An aryl peak was also observed at δ 161.6 which was consistent with the formation of the Ti-C(aryl) bond. These data were consistent with triple C-H activation and formation of the desired CCC-NHC pincer bis(dimethylamido) complex. An extraneous peak at δ 2.2 was always observed in the final product. No aromatic toluene peaks observed in the ^{1}H NMR, thus the peak

was attributed to dimethylamine. Complex **7** was washed more times with various solvents, and placed under reduced pressure at high temperatures, yet the excess dimethylamine could not be removed. Imidazolium salt **1** and the $Ti(NMe_2)_4$ were reacted under different conditions (THF at 100 °C and CH_2Cl_2 rt) to synthesize complex **7**, but upon work up the dimethylamine could not be removed. Elemental analysis was performed on complex **7**, but the data was not within acceptable range for the desired complex. This result was attributed to the extreme sensitivity of the complex to trace proton sources, in particular, humid air. Due to this result, elemental analyses of other similarly sensitive CCC-NHC pincer Ti complexes were not performed. Initial attempts at recrystallization of **7** employed CH_2Cl_2 and THF. After a prolonged period of time crystals formed. However, X-ray crystallography showed the crystals to be the (trichloro)Ti complex **8** (*vide infra*). This dimethylamido/halide ligand exchange had precedent, as the Zr analogue was known to undergo a dimethylamido/halide exchange affording the trihalide species when reacted with methyl iodide.[24] Bis(dimethylamido)(iodo)Ti complex **7** was later recrystallized from 1,2-dichlorobenzene and Et_2O, but the crystals crumbled when removed from the mother liquor. Addition of Paratone® to the mother liquor/crystal mixture also caused the crystals to crumble. Other solvent systems used to grow crystals such as; CH_2Cl_2/toluene or Et_2O, THF/toluene or ether did not yield crystalline product. Slow vapor diffusion of the same solvent systems at ambient or cold temperatures, also did not yield X-ray quality crystals.

Scheme 2.2.1.1 Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV), (**7**), and 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV), (**8**).

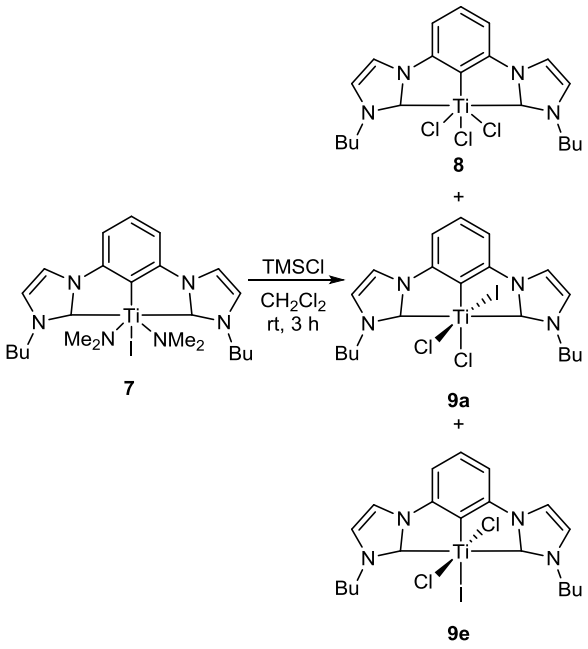


2.2.2 Synthesis and Characterization of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV), (8), and the geometric isomers 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(iodo) titanium(IV), (9a) and (9e)

After observing the stability of crystalline (trichloro)Ti complex **8**, it was hypothesized that a direct synthesis of **8** was possible by reacting the bis(dimethylamido)(iodo)Ti complex **7** with TMSCl (Scheme 2.2.2.1). As expected, the dimethylamido/halide exchange occurred rapidly upon exposure of complex **7** to TMSCl. The signal corresponding to the dimethylamido ligands of complex **7** was not observed in the ^{1}H NMR spectrum 1 h after TMSCl addition. New signals at δ 2.42 and δ 0.03 were observed, which corresponded to the expected side product, *N*-(trimethylsilyl)dimethylamine. The integral ratio of the signals at δ 2.42 and δ 0.03 was 6:9. This data provided evidence that the desired dimethylamido/halide reaction occurred. The

chemical shifts in the NMR spectra of the resulting complexes were similar to the chemical shifts of the (trichloro)Ti complex **8** crystals grown previously. However, the multiplicity of the signals in the ^{1}H NMR spectrum was too high to be one product or isomer. In particular, the asymmetric splitting of the signals corresponding to the methyl group of the butyl chain (δ 1.05 - 0.98) was the result of overlapping protons of different complexes. Furthermore, three unique doublets (δ 7.53, J = 1.8 Hz), (δ 7.49, J = 1.8 Hz) and (δ 7.45, J = 1.9 Hz) along with three unique doublets of doublets (δ 7.40, J_1 = 8.2 Hz, J_2 = 7.3 Hz), (δ 7.35, J_1 = 8.1 Hz, J_2 = 7.5 Hz), (δ 7.29, J_1 = 8.3 Hz, J_2 = 7.3 Hz) were observed in the aromatic region. These unique signals corresponded to the aryl/heteroaryl protons of three different complexes. Three unique sets of signals were observed in the ^{13}C NMR spectrum providing additional support for the assignment. Signals at δ 201.8, 197.1, and 194.5 were assignable as the carbene signals of three different complexes. One of the unique sets of aryl/heteroaryl signals previously described corresponded to the aryl/heteroaryl protons of complex **8**. Also, all of the carbon signals of complex **8** were observed in the ^{13}C NMR spectrum of the reaction. These observations were consistent with the formation of a small quantity of **8** upon reaction of **7** with TMSCl. The other sets of signals in the ^{1}H and ^{13}C NMR spectra were attributed to the axial and equatorial geometric isomers of the dichloro(iodo)Ti complex, **9a** and **9e**. The ratio of the geometric isomers was 3:1, though assignment of the major or minor isomer was not possible. The reaction depicted in Scheme 2.2.2.1 was carried out with excess TMSCl and prolonged reaction times in an effort to obtain only **8**. After 104 h, no changes were observed in the ^{1}H NMR spectrum of the reaction versus 1 h. Thus, the product isomer ratio of **8**:**9** major:**9** minor::3:6:2 appears to be the equilibrium ratio under these conditions.

Scheme 2.2.2.1 Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV), (**8**), and the geometric isomers 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(iodo) titanium(IV), (**9a**) and (**9e**).

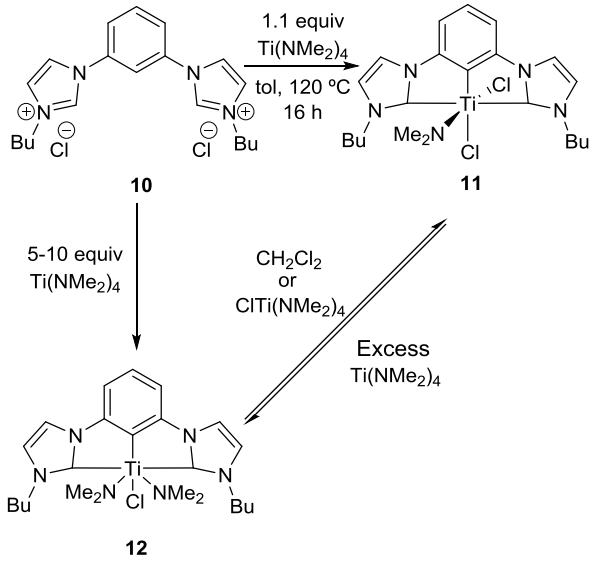


2.2.3.1 Synthesis and Characterization of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV) (11) and 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV) (12)

Since the reaction of bis(dimethylamido)(iodo)Ti complex **7** with TMSCl yielded a mixture of (trichloro)Ti complex **8** and mixed-halide dichloro(iodo)Ti complexes **9a** and **9e**, it became apparent that an efficient direct synthesis of the (trichloro)Ti complex **8** needed to avoid starting materials with iodide. Accordingly, bis(imidazolium) dichloride salt **10** was treated with 1.1 equivalents of freshly distilled $Ti(NMe_2)_4$ in toluene at 120 °C for 16 h (Scheme 2.2.3.1). The imidazolium proton signal at ($\delta \sim$ 10-11) disappeared along with the methylene signal at δ 4.42. A new signal was observed at δ 4.35 that was assigned to the methylene group α to the

nitrogen in the product. Additionally, the signal at δ 4.35 was a triplet of doublets, which was consistent with the Zr and Hf analogues.[25,26] The molecular structure of complex **11** as determined by X-ray crystal structure analysis is represented in Figure 2.2.5.2. The carbene signal was observed at δ 196.4 in the ^{13}C NMR spectrum. The signal corresponding to the Ti-C(aryl) bond was observed at δ 179.1. These data were consistent with the synthesis of dichloro(dimethylamido)Ti complex **11**.

Scheme 2.2.3.1 Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV), (**11**) and 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV), (**12**).



In a range of solvents and temperatures (CH_2Cl_2, 25 °C; THF, 100 °C; and toluene, 120 °C) chloro salt **10** was efficiently metallated with excess $Ti(NMe_2)_4$ to produce (chloro)bis(dimethylamido)Ti complex **12**, at bulk and NMR tube reaction scales (Scheme 2.2.3.1). No imidazolium proton signal was observed after the salt was treated with $Ti(NMe_2)_4$, and the signal for the methylene protons α to the nitrogen shifted to a triplet at δ 3.93 in the

metallated species. The observed triplet in the metallated species was attributed to rapid Ti amido exchange, similar to complex **7** (*vide supra*) and the bis(dimethylamido)(iodo)Zr complex.[24] A new dimethylamido peak was seen at δ 3.22 with an integration of 12H, which provided evidence for the synthesis of (chloro)bis(dimethylamido)Ti complex **12**. The ^{13}C NMR spectrum contained a signal at δ 189.9, which was assigned to the carbene carbon, and a signal at δ 161.2, which was attributed to the carbon of the Ti-C(aryl) bond. These data were consistent with assignment of the product as **12**. Removal of the volatiles followed by spectroscopic characterization of the crude product revealed exclusively complex **12** and the excess Ti amido reagents. After washing the crude product to remove the excess Ti amido reagents, variable amounts of dichloro(dimethylamido)Ti complex **11** were observed along with **12**, regardless of solvent used for washing (Et_2O, toluene). Additionally, observations of **12** in CD_2Cl_2 over time at room temperature revealed the formation of **11** (increase by 6% over 9 h). Furthermore, the ^1H NMR spectral analysis of the isolated product of the reaction of salt **10** with excess $Ti(NMe_2)_4$ taken in nonhalogenated CD_3CN contained a similar ratio of **11**:**12** (15:85), as the analysis in CD_2Cl_2 (17:83) of the same batch of material.

In an effort to minimize the formation of dichloro(dimethylamido)Ti complex **11** new strategies were employed. First the $Ti(NMe_2)_4$ was doubled to 10 molar excess to further favor complex **12** in the equilibrium. Additionally, the reaction was conducted in a mixture of CH_2Cl_2:toluene (5:1), and after 3 h it was flash cooled with liquid nitrogen in an attempt to freeze out the equilibrium and afford only bis(dimethylamido) product, **12**. The slurry was thawed at -47 °C and CH_2Cl_2 was removed under vacuum. The supernatant (toluene/excess Ti reagents) was decanted from the precipitated product. The precipitate was washed further at -78 °C with precooled toluene. $TiCl(NMe_2)_3$ remained as a contaminant of the isolated product even

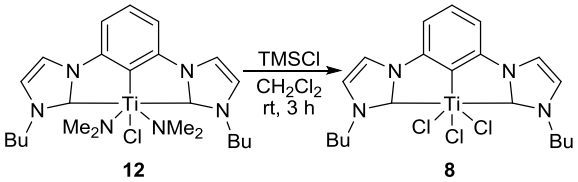
after numerous washes (8 × 5 mL) with toluene, at these low temperatures. Washing with THF (6 × 5 mL) also failed to remove the last traces of $TiCl(NMe_2)_3$ at these low temperatures. Employing this procedure yielded product that still contained a **11**:**12** mixture of ~15:85.

Consideration of all the experimental results led to the conclusion that **11** and **12** were in rapid equilibrium at room temperature even though **11** was not detectable by ^1H NMR spectroscopy in the crude material. Furthermore, **11** was much less soluble than **12** and was co-precipitating during isolation. Therefore, **11** precipitated preferentially from the crude material, even when it was not observable spectroscopically. As a result, the crude product was a mixture of **11**, **12**, and Ti amido reagents. When this crude product was dissolved in deuterated solvent for NMR spectroscopy, the equilibrium of **11** and **12** was in favor of **12** due to the excess $Ti(NMe_2)_4$. Thus, only **12** and Ti reagents were observed in the NMR spectrum of the crude product, while **11**, **12**, and Ti amido reagents were observed in the isolated product.

2.2.4 Direct Synthesis and Characterization of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (12)

(Chloro)bis(dimethylamido)Ti complex **12** was reacted with TMSCl to achieve a direct synthesis of (trichloro)Ti complex **8** (Scheme 2.2.4.1). The most obvious change in the ^1H NMR spectrum was a shift of the signal corresponding to the methylene group α to the nitrogen from δ 3.93 in complex **12** to δ 4.47 in complex **8**. The ^{13}C NMR spectrum contained a carbene signal at δ 194.5, and an aryl signal at δ 180.9 corresponding to the carbon of a Ti-C(aryl) bond. Both the ^1H and ^{13}C NMR spectra of the directly synthesized (trichloro)Ti complex **8** matched the spectra of the previously grown X-ray quality crystals obtained from **7** in CH_2Cl_2/THF. These data provided evidence for the efficient synthesis of (trichloro)Ti complex **8**, via this direct route.

Scheme 2.2.4.1. Synthesis of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**8**)

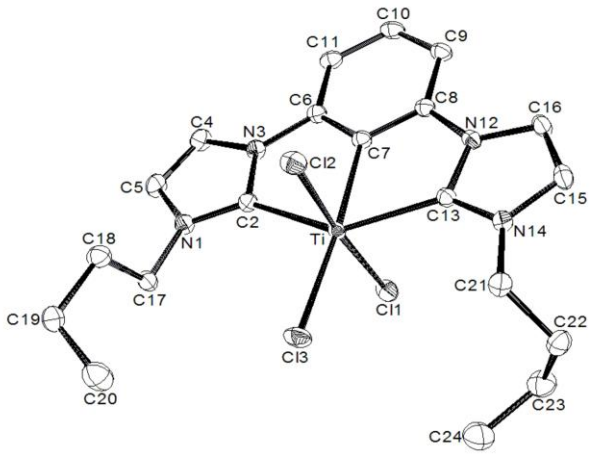


2.2.5 Molecular Structure Determination of Ti CCC-NHC Pincer Complexes

An ORTEP® plot of the molecular structure of (trichloro)Ti complex **8** is presented in Figure 2.2.5.1 along with selected metric data.[49] X-ray quality crystals of complex **8** were obtained from the initial attempt at the recrystallization of the bis(dimethylamido)(iodo)Ti complex **2** in CH_2Cl_2 and THF. The X-ray crystallography data confirmed the tridentate bonding of the CCC-NHC pincer ligand to the Ti(IV) center. The structure of complex **8** was a distorted octahedral center due to the meridional-coordination and constraints of the CCC-NHC pincer ligand. The N-heterocyclic carbene ligands occupied coordination sites trans to each other and had a C(NHC)-Ti-C(NHC) bond angle of 143.01(4)°. This bond angle was about 3° greater than the only other reported Ti(IV) metal complex containing an aryl or heteroaryl bridged bis(NHC) pincer ligand.[19] The Ti-C(NHC) bond lengths of complex **8** were 2.2192(10) Å and 2.2115(10) Å, which were less than 0.08 Å shorter than those in the CNC-NHC pincer Ti complex synthesized by Danopoulos.[19] The larger angle C(NHC)-Ti-C(NHC) angle was due to the shorter Ti-C(Aryl) distance (2.2610(10) Å) in **8**, versus the Ti-N(pyridyl) (2.332(5) Å) in the CNC pincer complex.[19] The Ti-C(aryl) bond was 2.1610(10) Å, which was within ± 0.08 Å of other similar Ti-C(aryl) bonds, incorporated into a pincer ligand.[50,51] Conversely, the Cl-Ti-Cl bond angle of (trichloro)Ti complex **3**, 174.506(13)°, was significantly larger than the Danopoulos pincer analogue's Cl-Ti-Cl bond angle of 161.42(7)°. The Ti-Cl bond lengths of

complex **8** (Ti-Cl(1) 2.3239(3) Å, Ti-Cl(2), 2.3119(3) Å, Ti-Cl(3), 2.3198(3) Å) were within ± 0.12 Å of known NHC pincer Ti metal complexes also containing a Ti-Cl bond.[19,23,34]

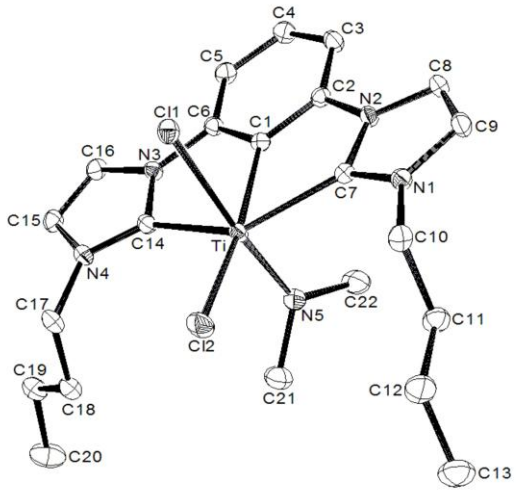
Figure 2.2.5.1 Molecular structure of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV), (**8**), selected bond lengths (Å) and angles (°): Ti-C(2), 2.2192(10); Ti-C(7), 2.1610(10); Ti-C(13), 2.2115(10); Ti-Cl(1), 2.3237(3); Ti-Cl(2), 2.3119(3); Ti-Cl(3), 2.3198(3); C(7)-Ti-C(2) = 71.51(4); C(7)-Ti-C(13) = 71.52(4); Cl(1)-Ti-Cl(2) = 174.506(13).



An ORTEP® plot of the molecular structure of complex **11** is presented in Figure 2.2.5.2 along with selected metric data.[49] Crystals of dichloro(dimethylamido)Ti complex **11** were grown from a solution of (chloro)bis(dimethylamido)Ti complex **12** in CH_2Cl_2. Similar to (trichloro)Ti complex **8**, the dichloro(dimethylamido)Ti complex **11** was found to have a distorted octahedral geometry with a C(NHC)-Ti-C(NHC) angle of 142.93(5)°, which was almost identical to **8**. This C(NHC)-Ti-C(NHC) bond angle was slightly larger than the Zr (136.40(11)°) and Hf (137.6(11)°) complexes synthesized under similar conditions, but within 3°

of the CNC-NHC pincer angle by (140.5(2)) reported by Danopoulos.[19,25,26] The larger angle C(NHC)-Ti-C(NHC) angle was again due to the shorter Ti-C(Aryl) distance (2.1593(14) Å) in **11**, versus the Ti-N(pyridyl) (2.332(5) Å) in the CNC pincer complex.[19] The Ti-C(aryl) bond of 2.1593(12) Å was within ± 0.08 Å of other similar Ti-C(aryl) bonds incorporated into a pincer ligand.[50,51] The Ti-C(NHC) bond lengths were 2.2406(14) Å and 2.2172(14) Å. The halide ligands of complex **11** occupied cis coordination sites and had a Cl-Ti-Cl bond angle of 86.725(15)°. The Ti-Cl bond lengths of complex **11** were 2.4725(4) Å and 2.3686(4) Å. The Ti-(dimethylamido) bond length was 1.9032(12) Å. These metric data were similar to previously reported Ti NHC complexes.[11,14,18-21,23,34]

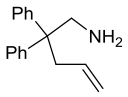
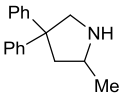
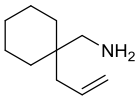
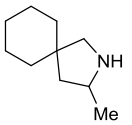
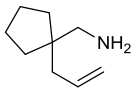
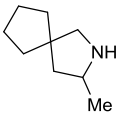
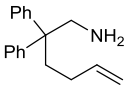
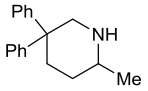
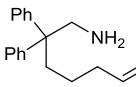
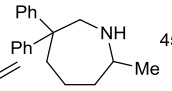
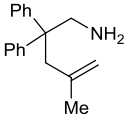
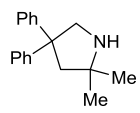
Figure 2.2.5.2. Molecular structure of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV), **11**, selected bond lengths (Å) and angles (°): Ti-Cl(1), 2.4725(4); Ti-Cl(2), 2.3686(4); Ti-N(5), 1.9032(12); Ti-C(1), 2.1593(14); Ti-C(14), 2.2406(14); Ti-C(7), 2.2172(14); C(1)-Ti-C(7) = 71.44(5); C(1)-Ti-C(14) = 71.76(5); C(7)-Ti-C(14) = 142.93(5).



2.2.6. Catalytic Results

Catalytic hydroamination/cyclization is a highly atom-economical method to synthesize new C-N bonds. The subsequent nitrogen containing heterocycles produced by the reaction are prevalent in naturally occurring and/or biologically active molecules.[52-55] Numerous metals have been employed for catalytic hydroamination/cyclization; however, group 4 complexes have been advantageous over late-transition metals due to their low cost and low toxicity.[56-59] Group 4 hydroamination catalysts are also advantageous over organolanthanide catalysts due to their enhanced stability and functional group tolerance.[58,60,61] It was previously reported that the CCC-NHC pincer Zr and Hf analogues were efficient catalysts for hydroamination/cyclization.[25,26] Therefore, the catalytic activities of bis(dimethylamido)(iodo)Ti complex **7** and (chloro)bis(dimethylamido)Ti complex **12** in hydroamination/cyclization was evaluated under conditions similar to the previous reports to allow comparison.[25,26] The best results for complexes **7** and **12** were achieved with substrates containing two phenyl substituents or a spirocyclohexane substituent (entries 1 and 2). Having a spirocyclopentane substituent on the substrate significantly decreased catalytic activity (entry 3). Complex **7** catalyzed the synthesis of piperidines in good yield, while complex **12** showed almost no activity (entry 4). However, 7-membered rings were not generated by either catalyst (entry 5). Complexes **7** and **12** were observed to have limited catalytic activity toward the cyclization of internally substituted alkenes (entry 6). In every case, complex **7** outperformed complex **12**, yet both were not as fast as the Zr and Hf analogues.[25,26] It is of note that the reaction temperature of 160 °C was need for the reaction. It was observed in experiments done at 150 °C that no reaction occurred.

Table 2.2.6.1 Substrate survey of hydroamination/cyclization catalytic activity of complexes **7** and **12**.

Entry	Amine	Heterocycle	**7**[Ti-I][a]		**12**[Ti-Cl][a,b]	
			Time	Conv (%)[c]	Time	Conv (%)[c]
1			96 h	91%	96h	67%
2			67 h	98%	69 h	26%
3			67 h	14%	45 h	7%
4			93 h	80%	72 h	4%
5			45 h	0%[d]	51 h	0%[d]
6			96 h	47%	69 h	11%

[a] 5 mol% catalyst in toluene-d_8 at 160 ºC.
[b] Entries 1-4, catalyst used 86% **7** by ^{1}H NMR spectroscopy, Entries 5-6, catalyst used 34% **7** by ^{1}H NMR spectroscopy.
[c] Conversions determined by ^{1}H NMR spectroscopy.
[d] No reaction.

2.3 Conclusion

In conclusion, CCC-NHC pincer Ti complexes have been synthesized using the amine elimination pathway that exploits the basicity and electrophilicity of $Ti(NMe_2)_4$. The coordination spheres of these CCC-NHC pincer Ti complexes were manipulated by controlling the amount of $Ti(NMe_2)_4$ used. The reaction of an excess amount of $Ti(NMe_2)_4$ with the bis(imidazolium) diiodide salt **1** yielded bis(dimethylamido)(iodo)Ti complex **7**, which reacted with CH_2Cl_2 to afford (trichloro)Ti complex **8**. Complex **7** reacted with TMSCl to yield a mixture of (trichloro)Ti complex **8**, and both geometric isomers of dichloro(iodo)Ti complexes

9a and **9e**. The reaction of the bis(imidazolium) dichloride salt **10** with a stoichiometric amount of $Ti(NMe_2)_4$ yielded dichloro(dimethylamido)Ti complex **11**, while reacting bis(imidazolium) dichloride salt **10** with an excess amount of $Ti(NMe_2)_4$ yielded (chloro)bis(dimethylamido)Ti complex **12**. An efficient synthesis of (trichloro)Ti complex **8** was accomplished by the reaction of (chloro)bis(dimethylamido)Ti complex **12** with TMSCl. Bis(dimethylamido)Ti complexes **7** and **12** were found to catalyze the hydroamination/cyclization of unactivated primary alkene-amines.

2.3 Experimental Section

General Consideration. Standard inert atmosphere techniques were used unless stated otherwise. Et_2O, toluene, and CH_2Cl_2 were degassed with argon and passed through two columns of activated alumina.[62] TMSCl was purified by distillation from triethylamine. Tetrakis(dimethylamido) titanium(IV) was purchased from Sigma Aldrich and purified by distillation under reduced pressure. CD_2Cl_2, and toluene-d_8 were purchased from Cambridge Isotopes and passed through a column of activated basic alumina. DMSO-d_6 was purchased from Cambridge Isotopes and used as received. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance 300 MHz or a Bruker Avance DRX 500 MHz NMR at ambient temperatures, unless otherwise stated. The ^1H NMR spectra were referenced internally from the residual protio-solvent signal: CD_2Cl_2 (δ 5.32), DMSO-d_6 (δ 2.50), and toluene-d_8 (δ 2.09). The ^{13}C NMR spectra were referenced internally using the signal from the deuterated solvent: CD_2Cl_2 (δ 54.0), DMSO-d_6 (δ 39.51), and toluene-d_8 (δ 20.4).

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV) (7). 1,3-bis(3-butylimidazol-1-yl)benzene diiodide **1** (0.300 g, 0.519 mmol),[26] $Ti(NMe_2)_4$ (593 μL, 2.60 mmol), and 100 mL of

toluene were added to a Schlenk flask. The mixture was heated to 160 °C for 16 h. The mother liquor was decanted, and the dark brown/black oily precipitate was washed with toluene (3 × 50 mL). Volatiles were removed under reduced pressure affording **7** (0.286 g, 94%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.60 (d, *J* = 1.8 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.24 (s, 1H), 7.23 (s, 1H) 7.21 (s, 1H), 7.15 (s, 1H), 3.93 (t, *J* = 7.5 Hz, 4H), 3.23 (s, 12H), 1.72 (pseudo quintet, *J* = 7.6 Hz, 4H), 1.40 (sextet, *J* = 7.6 Hz, 4H), 0.99 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (300 MHz, CD_2Cl_2): δ 190.5, 161.6, 147.9, 132.3, 122.6, 115.8, 110.8, 51.6, 40.8, 34.1, 20.5, 14.2. Anal. Calcd for $C_{24}H_{37}IN_6Ti$; C, 49.33; H, 6.38; N, 14.38. Found: C, 43.25; H, 5.38; N, 9.88. The descrepancy in calculated and found EA is attributed to decomposition as complex **7** is highly senstive to trace proton sources, even humid air

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (8). 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV) **7** (0.300 g, 0.608 mmol), TMSCl (330. μL, 3.04 mmol), and CH_2Cl_2 (200 mL) were stirred at room temperature for 3 h. Volatiles were removed under reduced pressure to afford a crude brown/yellow solid. CH_2Cl_2 (24 mL) was added, and the mixture was passed through a 0.2 μm filter. Et_2O (10 mL) was added affording an orange crystalline precipitate. The crystalline precipitate was collected and washed with Et_2O (3 × 10 mL), and volatiles were removed under reduced pressure to afford **8** (0.054 g, 19%). X-ray quality crystals were grown from a saturated solution of **8** in CH_2Cl_2 layered with THF at room temperature. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.45 (d, *J* = 1.9 Hz, 2H), 7.29 (dd, J_1 = 8.3 Hz, J_2 = 7.3, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 2.0 Hz, 2H), 4.47 (t, *J* = 7.5 Hz, 4H), 2.01 (m, 4H), 1.48 (sextet, *J* = 7.5 Hz, 4H), 1.0 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (500 MHz, CD_2Cl_2): δ 194.5, 180.9, 144.1, 129.3, 120.8, 114.3, 110.5, 52.1, 34.1, 20.4, 14.1.

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (8) and (axial and equatorial) 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(iodo) titanium(IV) (9a and 9e). NMR Scale Reaction: 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV) **7** (0.012 g, 0.019 mmol), TMSCl (25 μL, 0.19 mmol), and CD_2Cl_2 (0.5 mL) were combined in an NMR tube and maintained at room temperature for 104 h. Large scale experiment: 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)bis(dimethylamido)(iodo) titanium(IV) **7** (0.180 g, 0.308 mmol), TMSCl (197 μL, 1.55 mmol), and CH_2Cl_2 (50 mL) were stirred at room temperature for 3 h. Volatiles were removed under reduced pressure to afford a red solid mixture of **9a**, **9e**, and **8** (0.17 g, 97%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.53 (d, J = 1.8 Hz, 0.33H, minor product), 7.49 (d, J = 1.8 Hz, 1H, major product), 7.45 (d, J = 1.9 Hz, 0.5H, **3**), 7.40 (dd, J_1 = 8.2 Hz, J_2 = 7.3 Hz, 0.17H, minor product), 7.35 (dd, J_1 = 8.1 Hz, J_2 = 7.5 Hz, 0.5H, major product), 7.29 (dd, J_1 = 8.3 Hz, J_2 = 7.3 Hz, 0.25H, **8**), 7.20-7.07 (m, 4H, overlapping of major, minor, and **8** products), 4.54-4.42 (m, 4H, overlapping of major, minor, and **8** products), 2.11-1.96 (m, 4H, overlapping of major, minor, and **8** products), 1.55-1.43 (m, 4H, overlapping of major, minor, and **8** products), 1.05-0.98 (m, 6H, overlapping of major, minor, and **8** products). ^{13}C{^{1}H} NMR (300 MHz, CD_2Cl_2): δ 201.8, 197.1, 194.5, 183.5, 181.8, 180.8, 145.3, 144.5, 144.1, 129.3, 129.2, 129.1, 120.7, 120.6, 120.5, 115.0, 114.6, 114.3, 110.5, 110.4, 110.3, 52.1, 52.0, 34.0, 33.7, 33.3, 20.5, 20.4, 20.3, 14.1.

Preparation of 1,3-bis(3-butylimidazol-1-yl)benzene dichloride (10). 1,3-Bis-(imidazolyl)benzene (2.0 g, 9.5 mmol),[26] 1-chlorobutane (20. mL, 190 mmol), and CH_3CN (100 mL) were added to a sealed flask. The mixture was heated to 160 °C for 24 h. The reaction was cooled to room temperature and a white solid precipitated. The mother liquor was decanted from

the solid. The solid was dissolved with CH_2Cl_2 and transferred to a Schlenk flask. All volatiles were removed under reduced pressure yielding **10** (3.2 g, 85%). ^{1}H NMR (DMSO-d_6, 300 MHz): 10.66 (s, 2H), 8.77 (s, 3H), 8.15 (s, 2H), 8.10 (s, 1H), 8.07 (s, 1H), 7.94 (t, J = 8.2 Hz, 1H), 4.30 (t, J = 7.1 Hz, 4H), 1.93 (m, 4H), 1.34 (sextet, J = 7.3 Hz, 4H) 0.94 (t, J = 7.3 Hz, 6H); ^{13}C{^{1}H} (DMSO-d_6, 300 MHz): δ 136.1, 135.8, 131.8, 123.5, 121.6, 120.9, 114.9, 49.2, 31.0, 18.8, 13.3. HRMS (MeOH, *m/z*): 359.2023 $[M\text{-}Cl]^+$

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV) (11). 1,3-bis(3-butylimidazol-1-yl)benzene dichloride **10** (0.300 g, 0.754 mmol), $Ti(NMe_2)_4$ (198 μL, 0.830 mmol), and toluene (150 mL) were heated at 120 °C for 16 h. The reaction was cooled to room temperature and a red solid precipitated. The mother liquor was decanted, and the red solid was washed with toluene (2 × 15 mL) and was dried under reduced pressure affording **11** (0.19 g, 48%). X-ray quality crystals of **11** were obtained from the attempted recrystallization of **12** in CH_2Cl_2. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.41 (d, J = 1.7 Hz, 2H), 7.16 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 1.7 Hz, 2H), 7.00 (s, 1H), 6.97 (s, 1H), 4.35 (td, J_1 = 7.5 Hz, J_2 = 2.2 Hz, 4H) 3.40 (s, 6H) 1.89 (m, 4H), 1.45 (sextet, J = 7.5 Hz, 4H) 0.99 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} (300 MHz, CD_2Cl_2): δ 196.4, 179.1, 144.7, 128.0, 121.0, 114.6, 109.8, 51.5, 50.3, 35.0, 20.3, 14.1.

Preparation of 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)(chloro)bis(dimethylamido) titanium(IV) (12). 1,3-bis(3-butylimidazol-1-yl)benzene dichloride **10** (0.260 g, 0.654 mmol), $Ti(NMe_2)_4$ (747 μL, 3.26 mmol), and toluene (200 mL) were heated at 120 °C for 16 h. The reaction was cooled to room temperature and a fine red solid precipitated. The mother liquor was decanted and the red solid was washed with toluene (2 × 20 mL). Volatiles were removed under reduced pressure affording **12** (0.170 g,

48%). Second procedure: 1,3-Bis(1-butylimidazol-3-yl)benzene dichloride **10** (0.200 g, 0.502 mmol), $Ti(NMe_2)_4$ (599 μL, 2.51 mmol), and toluene (100 mL) were heated at 120 °C for 16 h. Volatiles were removed under reduced pressure. The red/brown product was washed with Et_2O (2 × 30 mL) and the volatiles were removed under reduced pressure, affording **12** (0.19 g, 70%). Third Procedure: 1,3-bis(3-butylimidazol-1-yl)benzene dichloride **10** (0.10 g, 0.25 mmol), $Ti(NMe_2)_4$ (590 μL, 2.5 mmol), CH_2Cl_2 (5 mL), toluene (1 mL) were stirred at ambient temperatures for 4 h. The reaction was flash frozen in liquid nitrogen under postive Ar. The reaction was allowed to warm to -47 °C where the CH_2Cl_2 removed under reduced pressure, precipitating a red solid. The mother liquor was decanted at -47 °C and the red solid was cooled to -80 °C. The red solid was washed with toluene (8 × 5mL) precooled to -80 °C. The volatiles were removed under reduced pressure at ambient temperature affording **12** (0.05 g, 37%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.70 (d, J = 1.8 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 7.23 (s, 2H), 3.93 (t, J = 7.5 Hz , 4H), 3.22 (s, 12H), 1.72 (quintet, J = 7.5 Hz, 4H), 1.41 (quartet, J = 7.5 Hz, 4H), 0.99 (t, J = 7.3 Hz, 6H); $^{13}C\{^1H\}$ (300 MHz, CD_2Cl_2): δ 189.9, 161.2, 147.4, 131.8, 122.0, 115.4, 110.4, 51.0, 40.3, 33.5, 20.0, 13.5.

The experimental procedures for X-ray Crystallography were written and reproduced with permission from by Professor Edward J. Valente.

X-ray Crystallography

The structures of complexes **8** and **11** were solved by direct methods in SHELXS-97.[63] All non-H atoms were found in the E-map. Refinements were done using SHELXL-97.[64] All non-H atoms were refined with anisotropic librational factors. H-atoms were observable in difference electron density maps, and placed in idealize positions; all were refined as riding

atoms with relative isotropic displacement parameters of 120% of the U(eq) of the attached atom.

Crystals of complex **8** were immersed in fluorocarbon oil. The specimens were bright red-orange, and a specimen (about 0.3 x 0.3 x 0.3 mm) was removed quickly, determined to be birefringent and essentially a single crystal by microscopy, and snagged with a small nylon loop, and transferred to the goniostat already cooled to 150 K.[65] The crystallographic properties and data were collected using Mo Kα radiation and the charge-coupled area detector (CCD) detector on an Oxford Diffraction Systems Gemini S diffractometer at 150 K.[65] A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. Data collection was carried out using Mo Kα radiation (graphite monochromator) with 8 runs consisting of 676 frames with a frame time of 8.7 s and a crystal-to-CCD distance of 50.000 mm. The runs were collected by omega scans of 0.8 degree width, and at detector position of 28.624, -30.343° in 2θ. The intensity data were corrected for absorption with an analytical correction.[66] Final cell constants were calculated from 16033 stronger reflections from the actual data collection after integration.

The crystal of complex **8** was monoclinic. The space group was $P^2(1)/n$ as determined from the cell geometry, systematic absences, reflections statistics, and successful solution and refinement. There were no solvent molecules, and a molecular complex comprises the asymmetric unit. The final full-matrix least-squares refinement converged to $R_1 = 0.0237$ (5491 reflections, F^2, $I > 2\sigma(I)$); $R_1 = 0.0302$ and $wR_2 = 0.0593$ for all 6520 unique data, 253 parameters, 0 restraints, goodness-of-fit (S) = 1.003 , and no extinction.

The asymmetric unit of complex **8** consisted of a six-coordinated titanium (IV) complex with the ligand engaged in three contacts with Ti, and one equatorial Cl and two axial Cl's. Butyl side chains were ordered. All distances and angles were within normal ranges.

Crystals of complex **11** were a deep red-brown solid in a sealed NMR tube filled with fluorocarbon oil as protectant from air/water. This protectant was wise, since on exposure to the air even in fluorocarbon oil, the substance slowly becomes colorless from the exterior of the crystal to the interior. Small prisms were in the sample, and a suitable single crystal of **11** was selected (0.089 x 0.310 x 0.455 mm), which was adhered to a nylon loop with fluorocarbon oil; the loop was epoxied to a stout glass fiber mounted on a pin; the pin was placed on a goniometer head. The crystallographic properties and data were collected using Mo Kα radiation and the charge-coupled area detector (CCD) detector on an Oxford Diffraction Systems Gemini S diffractometer at 101.2 K.[65] A preliminary set of cell constants was calculated from reflections observed on three sets of 5 frames which were oriented approximately in mutually orthogonal directions of reciprocal space. Data collection was carried out using Mo Kα radiation (graphite monochromator) with 4 runs consisting of 270 frames with a frame time of 30.00 s and a crystal-to-CCD distance of 50.000 mm, and a strategy to achieve a resolution of 0.7Å. The runs were collected by omega scans of 1.0° width, and at detector position of 28.468 and -30.187° in 2θ. The intensity data were corrected for absorption with an analytical correction.[66] Final cell constants were calculated from 6347 stronger reflections from the actual data collection after integration.

The crystal of complex **11** was orthorhombic, space group $P^2(1)/n$ as determined from the cell geometry, reflections statistics, systematic absences, and successful solution and refinement. This cell would require that a molecule comprise the asymmetric unit, which was what was

found, and lacking any solvation. All atom positions were ordered. The final full-matrix least-squares refinement converged to $R_1 = 0.0311$ (4879 reflections, F^2, $I > 2\sigma(I)$); $R_1 = 0.0538$ and $wR_2 = 0.0658$ for all 7288 data, 271 parameters, 0 restraints, goodness-of-fit (S) 0.955, and no extinction. Data were included to $2\theta = 61°$.

Molecules of complex **11** comprised the asymmetric unit, with four molecules in the cell. A central titanium was six coordinated, with bonds to two chlorides, one dimethylamido nitrogen and the three carbons of the CCC-NHC pincer ligand.

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CHAPTER 3

SYNTHESIS, CHARACTERIZATION, AND X-RAY MOLECULAR STRUCUTRE OF TANTALUM CCC-N-HETEROCYCLIC CARBENE PINCER COMPLEXES WITH IMIDAZOLYL AND TRIAZOLYL BASED LIGANDS

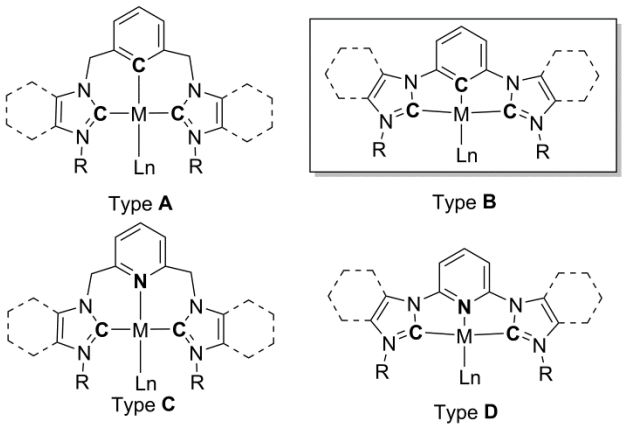
3.1 Research Background

Since their discovery, stable carbenes have had widespread application in transition-metal chemistry.[1-8] N-heterocyclic carbenes (NHCs) and their variants have become ubiquitous in late-transition-metal chemistry with applications in photoluminescence,[9-11] olefin metathesis,[5] C-C coupling,[11-13] and hydrosilylation.[14] Conversely, early-transition metal NHC complexes have yet to be explored to the same depth. Group 5 NHC metal complexes are particularly scarce. Fryzuk has reported the only four crystal structures of Ta complexes bearing an NHC ligand. No triazole-based-NHCs as ligands for groups 3, 4, or 5 metal centers have been, to our knowledge, reported previously. Reports of Ta NHC chemistry remain sparse despite significant reactivity with Ta which includes N_2 activation,[15-23] CO_2 activation,[24-26] chiral hydroaminoalkylation,[27] and

C-N bond activation.[28,29] New ligand architectures often lead to improved properties or new reactivity; therefore, the development of methodologies to access novel systems remains significant.

The pincer ligand architecture is an important class of tridentate, meridional binding ligands that form robust metal complexes.[30-32] Pincer ligands have application in a variety of reactivity;[33-36] noteworthy examples include C-F bond activation,[37,38] alkane dehydrogenation,[32] and catalytic C-C bond formation.[31] One of the reasons for the widespread use of pincer ligands is the ability to vary the lateral donor groups, providing an effective way to alter the properties of the metal center. Accordingly, incorporation of NHCs into pincer ligands has become of increasing interest.[31,39-44] Although pincer complexes have been known since the 1970s,[45-48] only a few examples of Ta pincer complexes have been reported.[49-54] Herein, we report an efficient route to synthesize CCC-NHC pincer Ta complexes with imidazole and triazole-based-NHC ligands.

Scheme 3.1.1 Metal Complexes Derived from Aryl-Bridged Bis(NHC)-Pincer Ligands.



Since the original report of Type B bis(NHC) pincer ligands (Scheme 3.1.1),[55] several groups worldwide have continued developing this class of ligand.[9,39,56-67] Use of early-transition-

metal amido starting materials to activate ligand precursors via amine elimination is an effective route to synthesize complexes bearing multidentate ligands.[23,68-77] In particular, this methodology has yielded a facile route for the synthesis of group 4 CCC-NHC pincer complexes. The electrophilicity of the d^0 metal center in conjunction with the basicity of the dimethylamido ligands were exploited to facilitate the necessary triple C-H bond activation of the imidazolium salt precursor. In the present work, this triple C-H bond activation methodology is successfully extended to Ta.

3.2 Results and Discussion

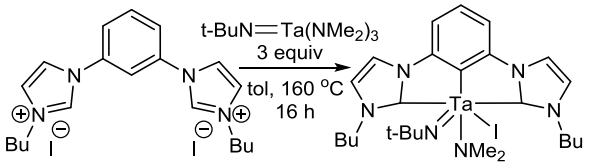
3.2.1 Synthesis and Characterization of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (13)

In direct analogy with the previous work synthesizing group 4 CCC-NHC pincer complexes,[55,60-62] $Ta(NMe_2)_5$ was first evaluated as a metalating reagent for imidazolium salt **1**. No imidazolium signal (δ 11.27) was observed in the ^{1}H NMR spectrum, indicating successful metalation after reacting $Ta(NMe_2)_5$ with imidazolium salt **1**. However, an abundance of signals suggested multiple coordination spheres at Ta. These materials were never found to be tractable. It was reasoned that the requisite high coordination number prevented clean isolation with this ligand set. Therefore, a Ta reagent that would reduce the coordination number of the products was sought. (*t*-Butylimido)tris(dimethylamido)tantalum(V), which contains a dianionic ligand, proved to be a solution to the problem. Thus, bis(imidazolium) diiodide salt **1** was reacted with excess (*t*-butylimido)tris(dimethylamido)tantalum(V) in toluene at 160 °C for 16 h yielding complex **13** (Scheme 3.2.1.1). As before, no imidazolium signal at δ 11.27 was observed in the ^{1}H NMR spectrum. Furthermore, the signal corresponding to the methylene group α to the nitrogen shifted from a triplet at δ 4.46 in salt **1** to a multiplet at δ 4.13. Unlike the previously

reported group 4 complexes, the dimethylamido signals of **13** were diasterotopic. Two unique singlets at δ 4.24 and δ 3.89 corresponding to the dimethylamido ligand were observed, which was the first time magnetically inequivalent methyl groups were observed in CCC-NHC pincer complexes. This phenomenon has been observed in other Ta complexes.[78] The carbene peak at δ 199.2 in the ^{13}C NMR spectrum also indicated successful metalation of the salt. An aryl peak was observed at δ 174.8, which was consistent with the formation of the Ta-C(aryl) bond. These data supported triple C-H activation and formation of the desired Ta CCC-NHC pincer complex.

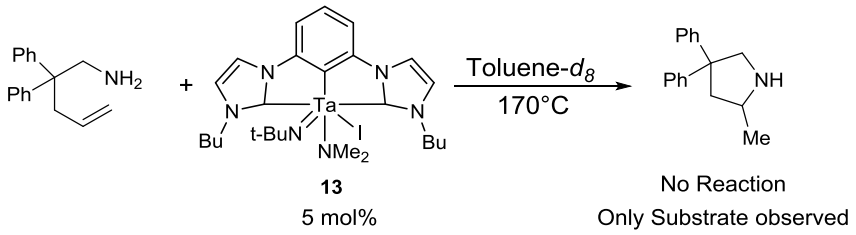
VT-NMR experiments were performed in an attempt to find the temperature at which the signals for the dimethylamido ligand would coalesce. After heating **13** to 382 K (109 °C) in d_8-toluene two diasterotopic signals were still observed for the dimethylamido ligand. From spin saturation transfer experiments the free energy of activation for the rotation ($\Delta G^{\ddagger}_{expt}$) is estimated to be 23.5 kcal mol^{-1}. This data is in reasonable agreement with results from PBEPBE DFT computations ($\Delta G^{\ddagger}_{comp}$ 25.8 kcal mol^{-1}).

Scheme 3.2.1.1 Synthesis of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).



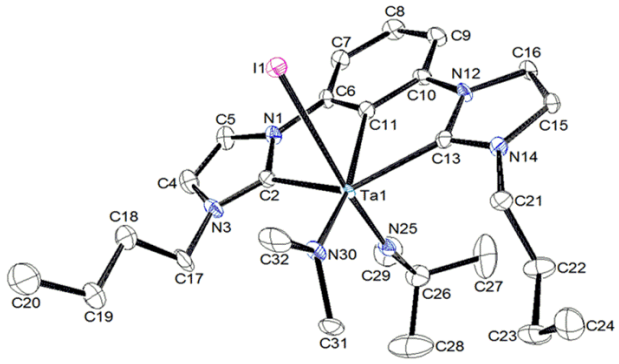
1 **13**

Scheme 3.2.2.1 Attempted Catalytic Hydroamintion/Cyclization Using (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).



X-ray quality crystals of Ta complex **13** were grown from a saturated benzene solution. An ORTEP® plot of the molecular structure of Ta complex **13** is presented in Figure 3.2.1.1 along with selected metric data. X-ray crystallographic data confirmed the tridentate bonding of the CCC-NHC pincer ligand to the Ta(V) center. Complex **13** has distorted octahedral coordination due to the constraints of the pincer ligand. The NHC ligands occupied coordination sites trans to each other and had a C^{NHC}-Ta-C^{NHC} bond angle of 139.1(2)°. The Ta-C^{NHC} bond lengths were 2.258(6) Å and 2.255(5) Å, comparable (±0.152 Å) to the Ta-C^{NHC} bond lengths of Fryzuk's complexes.[23] The Ta-C^{aryl} bond length was 2.248(5) Å, which was within 0.1 Å of other Ta pincer complexes with a similar aryl group flanked by neutral donors.[51,79] With a bond length of 1.794(5) Å, the Ta-N^{imido} bond was 0.07 Å longer than another reported Ta complex containing a linear *t*-butylimido ligand trans to a halogen.[80] The Ta-N^{amido} bond was 2.036(4) Å, which was within 0.07 Å of previously reported Ta pincer complexes.[50] At 3.0669(4) Å, the Ta-I bond length of **13** was much longer than other reported Ta-I bond.[81-89] The unusually long length of the Ta-I bond is attributed to the large trans-influence of the imido ligand.[90]

Figure 3.2.1.1 Molecular structure of complex **13** (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido) (dimethylamido)iodo tantalum(V). Hydrogens omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Ta(1)-C(2), 2.258(6); Ta(1)-C(13), 2.255(5); Ta(1)-C(11), 2.248(5); Ta(1)-N(25), 1.794(5); Ta(1)-N(30), 2.036(4), Ta(1)-I(1), 3.0669(4); C(2)-Ta(1)-C(13), 139.1(2); C(11)-Ta(1)-C(2), 69.6(2); C(11)-Ta(1)-C(13), 69.6(2).

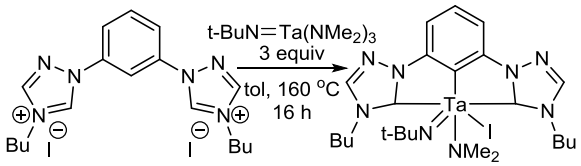


3.2.2 Synthesis and Characterization of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (15)

Research into late-transition-metal triazole-based-NHC has been established,[11,13,91-97] yet no early-transition-metal (group 3, 4, or 5) triazole-based-NHC complexes have been reported. Recently, the synthesis of a CCC-NHC triazolium pincer ligand precursor and its metalation to yield Ag NHC complexes was reported.[98] Based on the successful metalation of the imidazolium based CCC-NHC ligand precursor with *t*-(butylimido)tris(dimethylamido)-tantalum(V), the CCC-NHC triazolium pincer ligand precursor **14** was evaluated. Accordingly, upon reaction in toluene at 160 °C, a product with no triazolium signal in the ^{1}H NMR spectrum was obtained (Scheme 3.2.2.1). In direct parallel to complex **13**, the methylene group α to the nitrogen shifted

to δ 4.21 from δ 4.52 in triazolium salt **14**. Diasterotopic singlets were observed for the methyl groups of the dimethylamido ligand at δ 4.31 and δ 4.00. The carbene signal was observed at δ 199.7 in the ^{13}C NMR spectrum. All these data were consistent with the synthesis of Ta CCC-triazole-based NHC complex **15**. It should also me noted complex **15** can be synthesized using THF as a solvent at 100 °C

Scheme 3.2.2.1 Synthesis of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (t-butylimido)(dimethylamido)iodotantalum(V) (**15**).



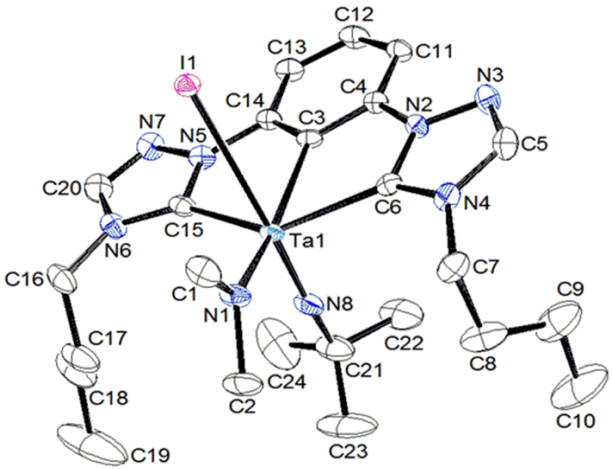
14 **15**

As early-transition metal complexes are known to catalyze hydroamination/cyclization of unactivated alkene amines, complex **13** was also evaluated for the same reactivity. Treating the diphenyl substituted substrate with **13** at typical conditions for hydroamination/cyclization yielded no reaction even after prolonged periods of time (34h at 160 °C). The reaction temperature was increased to 170 °C for 2 d, yet still no reaction was observed. It was determined that complex **13** was not catalytically active for the hydroamination/cyclization of unactivated alkene amine under these condition.

X-ray quality crystals of Ta complex **15** were grown by layering Et_2O onto a saturated toluene solution. An ORTEP® plot of one of the two molecules of Ta complex **15** found in the asymmetric unit is presented in Figure 3.2.2.1 along with selected metric data. The differences between the two molecules in the asymmetric unit were minor. No analogous bond lengths differed by more than 0.033 Å, nor did any analogous bond angles differ by more than 3.4°

between the two molecules. Full X-ray crystallographic data on both molecules is found in the X-ray crystallography section of chapter 3. For simplicity only the bond lengths and angles of the molecule illustrated in Figure 3.2.2.1 will be discussed. Like complex **13**, complex **15** was found to have a distorted octahedral geometry. The NHC ligands occupied coordination sites trans to each other with a bond angle of 138.69(11)°. With bond lengths of 2.286(3) Å and 2.283(3) Å, the Ta-C^{NHC} distances of complex **15** were comparable to **13** and Fryzuk's Ta NHC complexes. At 2.270(3) Å, the Ta-C^{aryl} bond length was consistent with other pincer Ta complexes (±0.12 Å) containing a similar aryl functionality flanked by neutral donors.[51,79] The Ta-N^{imido} bond length was 1.780(3) Å, which is within 0.06 Å of the only reported Ta complex containing a linear *t*-butylimido trans to a halogen.[80] With a bond length of 2.037(3) Å, the Ta-N^{amido} bond length was consistent with other Ta pincer complexes (±0.07 Å).[50] Complex **15** also had an unusually long Ta-I bond length of 3.0480(4) Å, similar to that of complex **13**.

Figure 3.2.2.1 Molecular structure of complex **15** (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodo tantalum(V). Only one formula unit shown and the hydrogens have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Ta(1)-C(6), 2.283(3); Ta(1)-C(15), 2.286(3); Ta(1)-C(3), 2.270(3); Ta(1)-N(1), 2.037(3); Ta(1)-N(8), 1.780(3); Ta(1)-I(1), 3.0480(4), C(6)-Ta(1)-C(15) 138.69(11); C(3)-Ta(1)-C(6), 89.10(11); C(3)-Ta(1)-C(15), 69.82(11).



3.3 Conclusion

In conclusion, unprecedented CCC-NHC pincer complexes of Ta have been synthesized via an amine elimination pathway. Use of $Ta(NMe_2)_5$ as a metalating reagent for imidazolium salt **1** yielded intractable products. Use of (*t*-butylimido)tris(dimethylamido)-tantalum(V) as a metalating reagent for imidazolium salt **1** lowered the coordination number and yielded a single isolable CCC-NHC Ta pincer complex. Recently reported triazolium salt **14** was treated likewise and yielded triazole-based CCC-NHC complex **15**. Complex **13** and **15** are only the fifth and sixth X-ray crystallographically determined molecular structures of Ta-NHC complexes. Furthermore, complex **15** is the first reported X-ray crystallographically determined molecular

structure of an early-transition-metal triazole-based-NHC complex. Further reactivity of complexes **13** and **15** will be reported in due course.

3.4 Experimental Section

General Consideration. Standard inert atmosphere techniques were used. Starting imidazolium and triazolium salts were prepared from previously reported literature references.[63,98] Et_2O and toluene were degassed with argon and passed through two columns of activated alumina.[99] Hexanes were purchased from Fisher Scientific, degassed with argon, and passed through a column of activated alumina prior to use. (*t*-Butylimido)tris(dimethylamido) tantalum(V) was purchased from Strem Chemicals and used as received. CD_2Cl_2, C_6D_6, d_8-toluene were purchased from Cambridge Isotopes and passed through a column of activated basic alumina prior to use. ^1H and ^{13}C NMR spectra were collected on a Bruker Avance 300 MHz NMR or Bruker Avance DRX 500 MHz NMR at ambient temperatures. The ^1H NMR spectra were referenced internally from the residual protio-solvent signal: CD_2Cl_2 (δ 5.32) and d_8-toluene (δ 2.09). The ^{13}C NMR spectra were referenced internally using the signal from the deuterated solvent: CD_2Cl_2 (δ 54.0).

Preparation of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (13). 1,3-Bis(3-butylimidazol-1-yl)benzene diiodide (**1**; 1.00 g, 1.73 mmol), (*t*-butylimido)tris(dimethylamido)tantalum(V) (1.99 g, 5.19 mmol), and toluene (200 mL) were heated at 160 °C for 16 h. The reaction was cooled to room temperature, and a white crystalline solid precipitated. The mother liquor was decanted, and the white crystalline solid was washed with toluene (3 × 10 mL) precooled to -78 °C. Volatiles were removed under reduced pressure affording **13** (1.16 g, 90%). X-ray quality crystals were obtained from cooling an NMR tube scale reaction in C_6D_6. ^1H NMR (300 MHz, CD_2Cl_2): δ

7.54 (d, J = 1.7 Hz, 2H), 7.19 (dd, J_1 = 8.6 Hz, J_2 = 6.6 Hz, 1H), 7.10 (d, J = 6.9 Hz, 2H), 7.09(d, J = 1.7 Hz, 2H), 4.24 (s, 3H), 4.13 (m, 4H), 3.89 (s, 3H), 1.99 (m, 4H), 1.48 (sextet, J = 7.5 Hz, 4H), 1.02 (t, J = 7.3 Hz, 6H), 0.70 (s, 9H) ; $^{13}C^{1}H$ (300 MHz, CD_2Cl_2): δ 199.2, 174.8, 146.7, 126.4, 121.7, 116.0, 109.3, 63.7, 59.7, 52.2, 33.8, 33.3, 20.9, 14.2. Anal. Calcd for $C_{26}H_{40}IN_6Ta$; C, 41.95; H, 5.42; N, 11.29 Found: C, 42.02; H, 5.45; N; 10.95.

Preparation of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (15). 1,3-Bis(3-butyltriazol-1-yl)benzene diiodide (**14**, 0.200 g, 0.345 mmol), (*t*-butylimido)tris(dimethylamido)tantalum(V) (0.397 g, 0.103 mmol), and toluene (10 mL) were heated at 160 °C for 16 h. The reaction was cooled to room temperature. The volatiles were removed under reduced pressure affording a brown crude product. This crude product was washed with hexanes 3 × 5 mL. Volatiles were removed under reduced pressure. The product was dissolved with 3 mL toluene and layered with 10 mL hexanes. A light brown solid precipitated from solution after 16 h. The mother liquor was decanted from the light brown solid. The light brown solid was triturated with hexanes (3 × 3 mL) and the volatiles were removed under reduced pressure affording **15**. (0.13 g, 51%). X-ray quality crystals were obtained by layering Et_2O onto a saturated solution in toluene. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.11 (s, 2H), 7.46 (d, J = 7.7 Hz, 2H), 7.27 (t, J = 7.7 Hz, 2H), 4.31 (s, 3H), 4.21 (t, J = 7.4 Hz, 4H), 4.00 (s, 3H), 2.04 (m, 4H), 1.49 (pseudosextet, J = 7.5 Hz, 4H), 1.04 (t, J = 7.4 Hz, 6H), 0.70 (s, 9H) ; $^{13}C\{^{1}H\}$ (300 MHz, CD_2Cl_2): δ 199.7, 171.0, 145.9, 142.7, 126.6, 111.6, 63.7, 60.4, 54.9, 50.0, 33.4, 33.1, 20.7, 14.0. Anal. Calcd for $C_{24}H_{38}IN_8Ta$; C, 38.62; H, 5.13; N, 15.01. Found: C, 37.25; H, 4.73; N, 13.91. Complex **15** is extremely sensitive to trace proton sources, even humid air. The calculated EA for the analogues complex of **15** where an (OH) replaces the (NMe_2) is C, 36.73; H, 4.62; N, 13.63. The calculated EA of

complex **15** where an (OH) replaces the (NMe_2) is in better agreement with the found EA. This data suggests partial hydrolysis of complex **15** during analysis**.**

The experimental procedures for X-ray Crystallography were written and reproduced with permission from by Mr. Henry Valle.

X-ray Crystallography

Experimental

Single crystals of $C_{26}H_{40}N_6ITa$ (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**) were crystallized via a saturated solution of complex **13** in benzene. A suitable crystal was selected and mounted on a 150um cryoloop and mounted on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2,[100] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using CGLS minimisation.[101]

Single crystals of $C_{48}H_{80}N_{16}I_2Ta_2$ (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodo tantalum(V) (**15**) were crystallized via layering Et_2O to a saturated solution in toluene. A suitable crystal was selected and mounted on a 150 um mitogen mount on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.13 K during data collection. Using Olex2,[100] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimisation.[101]

Crystal Data for $C_{26}H_{40}N_6ITa$ (M =744.49): monoclinic, space group $P2_1/c$ (no. 14), a = 14.3134(5) Å, b = 14.0461(5) Å, c = 14.6772(5) Å, β = 95.1620(10)°, V = 2938.85(18) $Å^3$, Z = 4, T = 100.15 K, μ(CuKα) = 15.326 mm^{-1}, *Dcalc* = 1.683 g/mm^3, 27074 reflections measured (6.2 ≤

$2\Theta \leq 139.862$), 5465 unique ($R_{int} = 0.0508$) which were used in all calculations. The final R_1 was 0.0491 ($I > 2\sigma(I)$) and wR_2 was 0.1370 (all data).

Crystal Data for $C_{48}H_{80}N_{16}I_2Ta_2$ (M =1492.95): triclinic, space group P-1 (no. 2), a = 10.6851(12) Å, b = 10.9572(12) Å, c = 24.299(3) Å, α = 89.884(1)°, β = 84.039(1)°, γ = 86.730(1)°, V = 2824.9(5) Å^3, Z = 2, T = 100.13 K, μ(N/A) = 5.010 mm^{-1}, *Dcalc* = 1.7550 g/mm^3, 34679 reflections measured ($3.38 \leq 2\Theta \leq 58.12$), 13751 unique ($R_{int} = 0.0301$) which were used in all calculations. The final R_1 was 0.0241 (I>=2u(I)) and wR_2 was 0.0617 (all data).

Free Energy of Rotation Calculation Using Spin Saturation Transfer: Using modifications of a procedure by Odom, the free energy of rotation of the dimethylamido ligand was calculated by NMR.[102] A saturated solution of **2** in d_8-toluene prepared at ambient temperature and was decanted from all solid for use in the spin saturation experiment. An 80% ethylene glycol/20% d_6-DMSO standard was used to measure the temperature of the NMR probe prior to the experiment. The sample was allowed to equilibrate to the desired temperature for 15 min. The 90° pulse width was determined and set at the desired temperature. A quality ^{1}H NMR spectrum was taken at the desired temperature. T_1 values of the dimethylamido ligand of **2** were determined using the inversion recovery method. The delay was set to $5 \times T_1$. The saturation power was set to 59 -dBW. An experiment was performed where the most upfield dimethylamido signal was saturated. A second experiment was performed where an equidistant offset point was saturation to ensure the decoupler sidebands did not overlap with the signal being studied for integration changes. The rate of exchange was then determined using the equation below. M_o is the integration without saturation, M_a is the integration with saturation, and T_1 is the relaxation time of the methyl signal most downfield.[102]

$$k_{obs} = \frac{1}{T_1}\left[\frac{M_o}{M_a} - 1\right]$$

Once the rate of exchange (k_{obs}) was determined the free energy of activation for the rotation was calculated using the Eyring equation below. *K* is the transmission coefficient assumed to be 1, k_b is the Boltzmann constant, T is temperature in Kelvin, h is Plank's constant, and R is the gas constant.[102]

$$k_{obs} = K\frac{k_B T}{h}e^{-\Delta G^{\ddagger}/RT}$$

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CHAPTER 4

SYNTHESIS AND CHARACTERIZATION OF TANTALUM CCC-NHC BIS(IMIDO) COMPLEXES

4.1 Research Background.

The seminal work of Bertrand and Arduengo has shown that carbenes are not always the transient intermediates as chemists once believed,[1-3] but can be persistent and bottleable carbon species. In particular, N-heterocyclic carbenes (NHCs) have become ever-present in late transition metal chemistry,[4] yet the study of early-transition metal NHCs is still in its infancy. [3] Group 5 NHC complexes are vastly understudied. Only 6 Ta NHC complexes have been reported to date.[5,6] As the popularity of NHCs as ancillary ligands for new metal complexes increased, so has research into new NHC variants.[7] One noteworthy NHC derivative is the imidazole-base-NHC bonded to the metal at the backbone C-4 or C-5 carbon, known as a mesionic carbene (MIC) or abnormal carbene. Crabtree reported the first MIC complex in

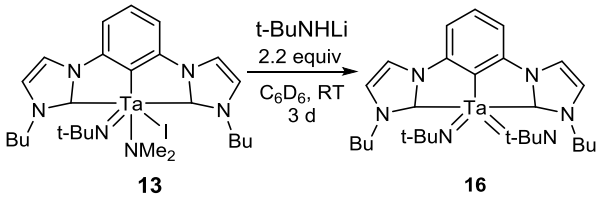
2001,[8] while the first free MIC was reported by Bertrand in 2009.[9] Bonding via C-4 or C-5 carbon makes MICs even better σ-donors than the C-2 bound NHCs. The increased σ-donor ability is due to the presence of only one adjacent heteroatom, which decreases the inductive effect on the carbene.[10] Robinson has further expanded alternative binding by imidazole-based NHCs with his recent report of imidazole ring containing simultaneous carbene centers at the C-2 and C-4 positions, known as the anionic N-heterocyclic dicarbene (NHDC).[11] Currently no MIC or NHDC complexes for early-transtion metals have been characterized by X-ray crystallography. Herein we report the synthesis of Ta CCC-NHC and CCC-NHC/NHDC bis(imido) complexes and their catalytic activity in oxidative amination.

4.2 Results and Discussion

4.2.1 Synthesis of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (16).

Following a similar synthetic procedure to synthesize Ta bis(imido) complexes using lithium amides by Wigley,[12,13] complex 13 was reacted with lithium *t*-butylamide in C_6D_6 at ambient temperature, on an NMR tube scale (Scheme 4.2.1.1). The most obvious change in the ^{1}H NMR spectrum from complex 13 in C_6D_6 to bis(imido) complex 16 in C_6D_6, was the loss of the dimethylamido signals at δ 4.42 and 4.41. The signal corresponding to the methylene group adjacent to the imidazolyl nitrogen shifted from diastereotopic multiplets at δ 3.87 and 3.69 in 13 to a pseudotriplet at δ 4.42 in 16. The signal at δ 1.65 with an integration of 18H corresponds to the two t-butylimido ligands, which is a great change from the *t*-butylimido signal of 1 found at δ 0.86 and having an integration of only 9H. The ^{13}C NMR spectrum contained a carbene peak at δ 201.8 and an aryl signal at δ 170.3. These data were consistent with the synthesis of a Ta CCC-NHC pincer bis(imido) complex.

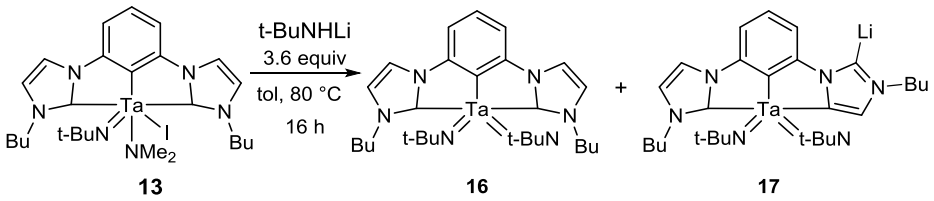
Scheme 4.2.1.1 Synthesis of (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**16**).



4.2.2 Synthesis of (1-(3-butylimidazol-1-yl-2-lithium-4-idene 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (17).

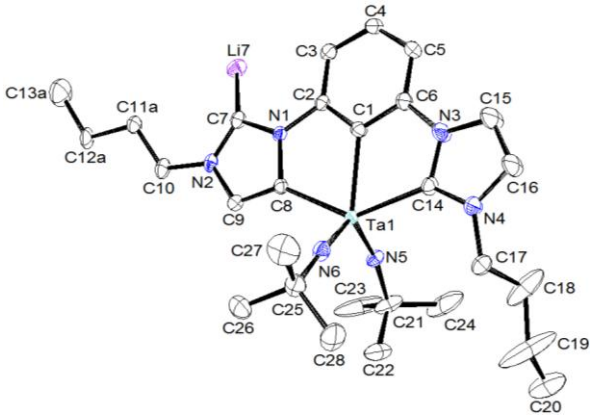
Upon increasing the reaction to bulk scale, problems with converting the starting material to the desired bis(imido) complex were observed. In an effort to convert all the starting material to the bis(imido) complex, the reaction was heated to 80 °C (Scheme 4.2.2.1). After isolating the product, a set of signals corresponding to a second Ta CCC-NHC pincer complex was observed. Two signals at δ 1.5 and δ 1.0, with integrations of 9H each, corresponded to the t-butyl signals of the *t*-butylimido ligands of the second Ta CCC-NHC pincer complex. The magnetic inequivalent *t*-butylimido ligands provided evidence that the second Ta CCC-NHC pincer complex was not symmetrical. This material was not soluble enough in C_6D_6 and d_8-toluene for signals to be observed in the ^{13}C NMR spectrum. The material reacted with other common deuterated solvents such as CD_3Cl, CD_2Cl_2, and CD_3CN. Consequently, no usable ^{13}C NMR data has been obtained to date. However, the molecular structure of the second pincer complex was confirmed as a Ta CCC-NHC/NHDC by X-ray crystallography.

Scheme 4.2.2.1 Synthesis of (1-(3-butylimidazol-1-yl-2-lithium-4-idene 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**).



X-ray quality crystals of Ta complex 17 were grown from layering a saturated toluene solution of 16 and 17 with hexanes. An ORTEP® plot of the molecular structure of Ta complex 17 is presented in Figure 4.2.2.1 along with selected metric data. X-ray crystallographic data confirmed the tridentate bonding of the CCC-NHC pincer ligand to the Ta(V) center. Complex 17 has distorted trigonal bipyramidal coordination due to the constraints of the pincer ligand. The NHC and MIC ligands occupied coordination sites trans to each other and had a C^{NHC}-Ta-C^{MIC} bond angle of 139.10(13)°. The Ta-C^{MIC} bond length was 2.277(4) Å. This unprecedented bond was comparable (-0.01 Å) to the other Ta-C^{NHC} bond length in pincer ligand which was 2.286(4) Å. Both the Ta-C^{MIC} and Ta-C^{NHC} were in agreement (±0.13 Å) with other known Ta-C^{NHC} bond lengths.[5,6] The Ta-C^{aryl} bond length was 2.282(5) Å, which was within 0.12 Å of other Ta pincer complexes with a similar aryl group flanked by neutral donors.[14,15] With a bond lengths of 1.866(4) Å and 1.825(4), the Ta-N^{imido} bonds were similar (±0.081 Å) to other reported Ta bis(imido) complexes.[12,13,16] At 117.67(19)°, the N^{imido}-Ta-N^{imido} angle was similar to other Ta bis(imido) angles.[13,16] The C(7)-Li(7) bond length was 2.117 Å, analogous to the Li-C^{NHC} bond length (-0.058 Å) of the free NHDC by Robinson.[11]

Figure 4.2.2.1 Molecular structure of complex 17 (1-(3-butylimidazol-1-yl-2-lithium-4-idene 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V). Only one formula unit shown and the hydrogens have been omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å) and angles (°): Ta(1)-C(1), 2.281(4); Ta(1)-C(8), 2.277(4); Ta(1)-C(14), 2.286(4), Ta(1)-N(5), 1.869(3); Ta(1)-N(6), 1.826(3); C(8)-Ta(1)-C(14), 139.10(13); C(1)-Ta(1)-C(14), 69.50(14); C(8)-Ta(1)-C(1), 69.69(13); N(6)-Ta(1)-N(5), 117.68.



4.2.2 Catalytic Oxidative Amination

The catalytic formation of cyclic imines from unactivated amino-alkenes (Oxidative Amination) is an extremely rare reaction. To date oxidative amination has only been seen with a Ru catalyst by Mitsudo and as a side product by Hartwig.[17,18] Treating bis(imido) complex 16 with the diphenyl substituted substrate (entry 1 Table 4.2.3.1) yielded the cyclic imine and the reduced substrate in a 50:50 ratio, no starting material was observed. Isolation of the crude product of catalysis was attempted, however the cyclic imine and saturated substrate product were found to eleut in the same fraction. Determination of the products was still possible. The spectral data (^{1}H NMR, ^{13}C NMR, and Mass Spectometry) matched the sum of the literature precedents for the products using the diphenyl substituted substrate. The oxidative amination catalysis was found to have catalytic activity with substrates containing a spirocyclopentane

(entry 2), spirocyclohexane (entry 3), and a phenyl and allyl substituent (entry 4) at the C-2 position. No signals for these substrates were observed after catalysis in the ^{1}H NMR spectrum. A signal around δ 173 was observed in the ^{13}C NMR spectra of the all these substrates (entries 2-4) after catalysis. This data suggests that the imine product is formed. The mass spectrum of the substrate with the phenyl and allyl substituent at the C-2 position of the substrate (entry 4) had signals at 200.1, 202.1, and 204.1 which suggest the products of catalysis were the protonated cyclic imine, protonated hydroamination, and protonated saturated substrate. Signals in the mass spectrum of the spirocyclohexyl substituted substrate (entry 2) had signals at 152.1 which corresponded to the cyclic imine product. The proposed products for entries 2-4 have no literature precedents. Separation and isolation of the products is currently underway. Once the products separated and isolated, accurate ratios of the amount of each product produced will can and will be reported. Furthuremore, substrates with a terminal or internal substituted double bond were found to have no reactivity with the catalyst (entries 6 and 8). Also, no reactivity was observed in substrates that formed 6-membered rings, nor indole substrates (entries 7 and 9). Catalytic oxidative amination was also performed with bis(imido) samples that contained Ta HNDC complex **17**, however no reaction was observed. 3,3-Dimethyl-1-butene was added as a hydrogen acceptor to produce only the cyclic imine product. Addition of this sacrificial olefin was found to impede all reactivity and only unreacted substrate was observed in the ^{1}H NMR spectrum.

Scheme 4.2.3.1 Oxidative Amination of unactivated alkene amines using (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V).

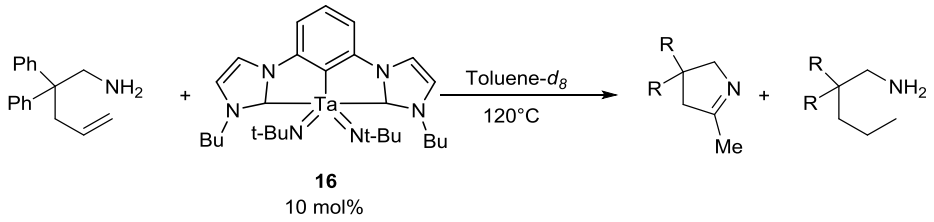
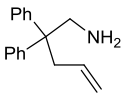
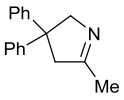
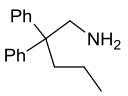
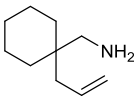
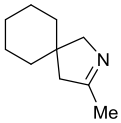
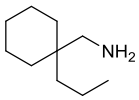
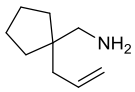
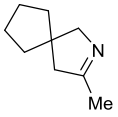
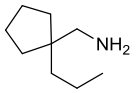
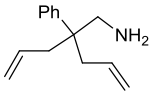
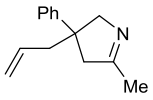
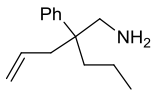
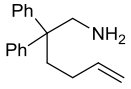
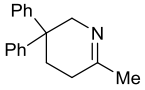
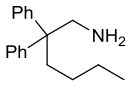
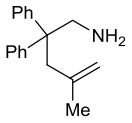
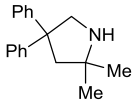
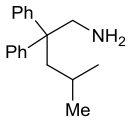
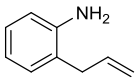
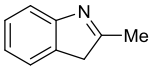
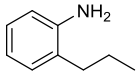
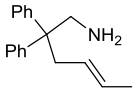
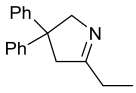
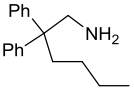
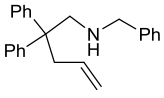
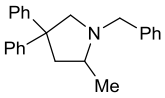
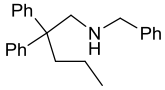
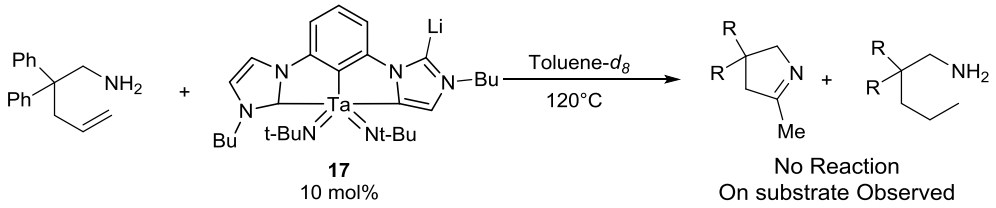


Table 4.2.3.1 Oxidative Amination of unactivated alkene amines.

Entry	Substrate	Proposed Imine Product	Proposed Reduced Product	Amount of substrate consumed
1[a]				100%
2				100%
3				100%
4				100%
5				No Reaction
6				No Reaction
7				No Reaction
8				No Reaction
9				No Reaction

[a] Sum if singals in isolated ^{1}H and ^{13}C NMR match literature precendnts for imine and reduced products

Scheme 4.2.3.1 Attempted Oxidative Amination of unactivated alkene amines using



4.3 Conclusion

In conclusion, unprecedented Ta CCC-NHC and CCC-NHC/NHDC bis(imido) complexes have been synthesized. Reacting Ta starting material **13** with lithium *t*-butylamide at ambient temperatures yielded the Ta CCC-NHC bis(imido) complex **16**. Upon increasing the reaction to bulk scale, problems converting all of staring material **13** to the desired bis(imido) complex were observed. In an effort to remedy this issue, excess lithium *t*-butylamide was added and the temperature of the reaction was increased to 80 °C. The resulting product of these changes in reaction condition was a mixture of Ta CCC-NHC complex **16** and Ta CCC-NHC/NHDC complex **17**. Novel NHDC complex **17** is the first X-ray crystallographically determined molecular structure of an early-transition-metal NHDC complex. Complex **16** was found to be catalytically active in converting unactivated amino-alkenes to a mixture of cyclic imines and the reduced substrate.

4.4 Experimental Section

General Consideration. Standard inert atmosphere techniques were used. Ta starting material **13** and lithium *t*-butylamide were synthesized according to previous reported literature references.[6,19] Solvents were degassed with argon, and passed through a column of activated alumina prior to use.[20] ^{1}H and ^{13}C NMR spectra were collected on a Bruker Avance 300 MHz

NMR or Bruker Avance DRX 500 MHz NMR at ambient temperatures. The ^{1}H NMR spectra were referenced internally from the residual protio-solvent signal: d_8-toluene (δ 2.09) C_6D_6 (δ 7.16). The ^{13}C NMR spectra were referenced internally using the signal from the deuterated solvent: C_6D_6 and (δ 128.39).

Preparation of Synthesis of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (16). NMR Scale Reaction: (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (0.025g, 0.0034 mmol), lithium *t*-butylamide (0.0058g, 0.074mmol), and C_6D_6 (0.5mL) were added to an NMR tube and maintained at ambient temperature for 3 days. ^{1}H NMR (300 MHz, C_6D_6): δ 7.04 (t, *J* = 7.7 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 1.8 Hz, 2H), 6.26 (d, *J* = 1.7 Hz, 2H), 4.42 (pseudotriplet, 4H), 1.77 (m, 4H), 1.65 (s, 18H), 1.37 (m, 4H), 0.95 (triplet, *J* = 7.4 Hz, 6H); ^{13}C{^{1}H} (300 MHz, C_6D_6): δ 201.8, 170.3, 149.6, 128.7-128.8 (signal overlaps with C_6D_6), 120.4, 115.6, 108.9, 64.3, 52.7, 51.8, 48.7, 38.8, 38.2, 37.4, 33.1, 32.5, 20.8, 14.4.

Preparation of Synthesis of (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (16) and (1-(3-butylimidazol-1-yl-2-lithium-4-idene 3-(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (17). (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (0.204g, 0.270 mmol), lithium *t*-butylamide (0.0470g, 0.60mmol), and toluene (10mL) were stirred at ambient temperature for 16 h. Additional lithium *t*-butylamide (0.030, 0.379 mmol) was added and the reaction was heated at 80 °C for 16 h. The volatiles were removed under reduced pressure. Toluene (10 mL) was added to the crude material in an attempt to dissolve the product. Pentane (8 mL) was layered on to the mixture to precipitate any product in solution. The mother liquor was removed and the product was washed with pentane (3×3 mL). Volatiles

were removed under reduced pressure to afford a mixture of **16** and **17** (0.06g, 34%). X-ray quality crystals of **17** were grown from layering pentane onto a saturated solution of **16** and **17**. ^{1}H NMR (300 MHz, d_8-toluene, sample not homogenous): δ 7.86 (broad s, 1H, **17**) 6.85 (broad s, 2H, **17**), 6.80 (broad s, 1H, **17**), 6.78 (broad s, 1H, **17**), 6.66 (broad s, 1H, **16**), 6.63 (broad s, 1H, **16**), 6.61(broad s, 1H, **16**) 6.27 (broad s, 2H, **16**), 6.25 (broad s, 1H, **17**), 4.40 (pseudotriplet, 5H, overlapping **16** and **17**), 4.04 (quartet, 3H, **17**), 1.76 (m, 11H, overlapping **16** and **17**), 1.60 (s, 9H, **17**), 1.56 (s, 18H, **16**), 1.44 (m, 6H, overlapping **16** and **17**) 1.32 (m, 6H, overlapping **16** and **17**) 0.08 (t, *J* = ,9H, overlapping **16** and **17**), 0.90 (t, *J* = overlapping **16** and **17**) 0.86 (s, 9H, **17**).

The experimental procedures for X-ray Crystallography were written and reproduced with permission from by Mr. Henry Valle.

X-ray Crystallography

Experimental

Single crystals of $C_{28}H_{43}N_6OTaF_{0.25}Cl_{0.25}Si_{0.25}Br_{0.25}Li_{0.25}$ 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**) were crystallized via layering pentane onto a saturated toluene solution of **16** and **17**. A suitable crystal was selected and placed on a 150 um cryoloop. X-ray crystallographic analysis was performed on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.08 K during data collection. Using Olex2,[21] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXS refinement package using Least Squares minimisation.[22]

Crystal Data for $C_{28}H_{43}N_6OTaF_{0.25}Cl_{0.25}Si_{0.25}Br_{0.25}Li_{0.25}$ (*M* =702.98): monoclinic, space group $P2_1/n$ (no. 14), *a* = 11.095(3) Å, *b* = 15.178(3) Å, *c* = 17.651(4) Å, *β* = 93.664(2)°, *V* = 2966.4(11) Å^3, *Z* = 4, *T* = 100.08 K, μ(MoKα) = 4.107 mm^{-1}, *Dcalc* = 1.574 g/mm^3, 34837

reflections measured ($3.542 \leq 2\Theta \leq 57.988$), 7427 unique ($R_{int} = 0.0503$) which were used in all calculations. The final R_1 was 0.0316 ($I > 2\sigma(I)$) and wR_2 was 0.0799 (all data).

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APPENDIX

X-ray Crystallography

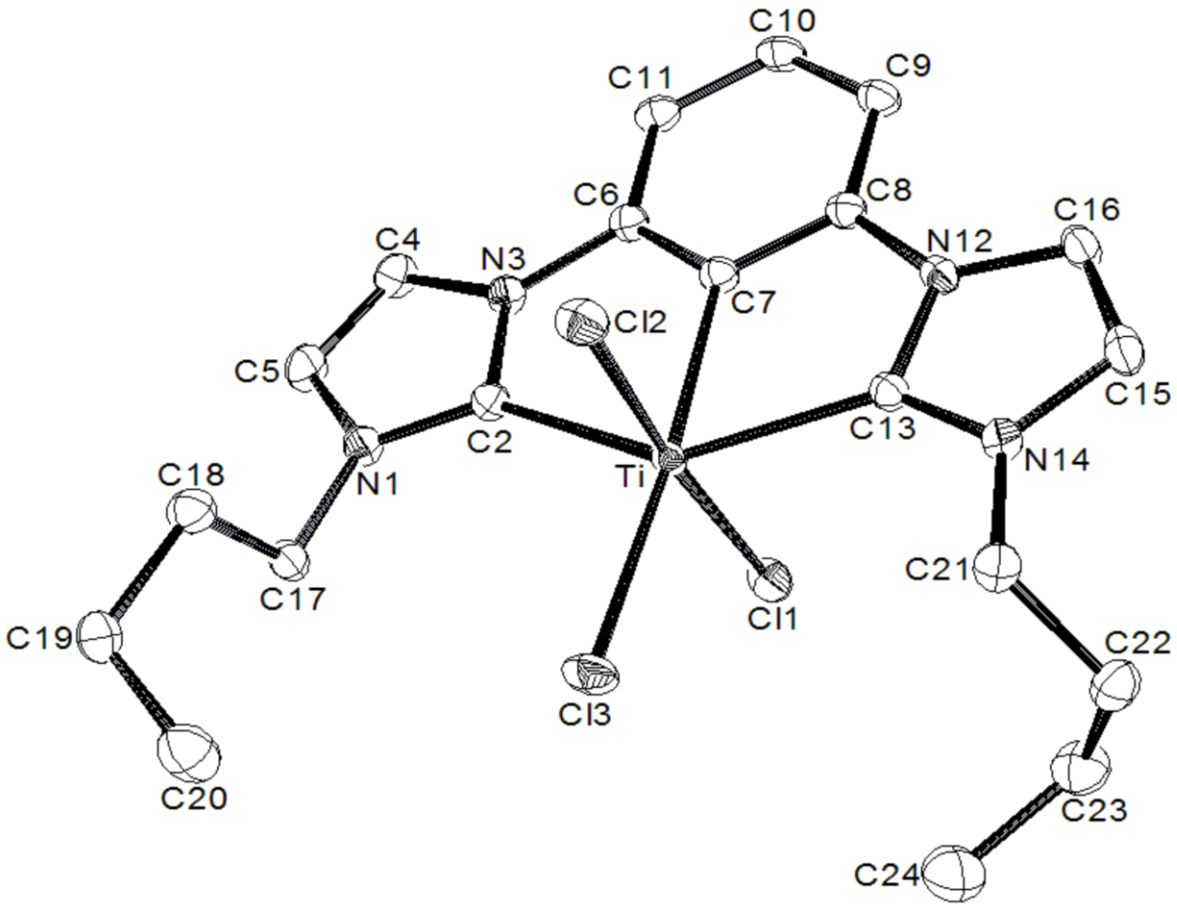


Figure A1. 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**3**).

Relevant Equations used in this report:

$$R_{int} = \Sigma\ |F_o^2 - < F_o^2 >| \ / \ \Sigma|F_o^2|$$

$$R_1 = \Sigma||F_o|-|F_c|| \ / \ \Sigma|F_o|$$

$$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] \ / \ \Sigma\ [w(F_o^2)^2]]^{1/2}$$

where $w = q \ / \ [\sigma^2\ (F_o^2) + (a*P)^2 + b*P + d + e*\sin(\theta)]$

$$GooF = S = [\Sigma[w(F_o^2-F_c^2)^2] \ / \ (n-p)]^{1/2}$$

Table A1-1. Crystal data and structure refinement for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**8**).

Empirical formula	$C_{20}H_{25}C_{l3}N_4Ti$
Formula weight	475.67
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P^2(1)/n$
Unit cell dimensions	a = 12.3079(3) Å $\alpha = 90^o$. b = 11.1195(2) Å $\beta = 105.153(2)^o$. c = 16.0997(4) Å $\gamma = 90^o$.
Volume	2126.76(8) $Å^3$
Z, Calculated density	4, 1.486 Mg/m^3
Absorption coefficient	0.793 mm^{-1}
F(000)	984
Crystal size	0.3 x 0.3 x 0.3 mm
θ range for data collection	3.29^o to 30.63^o.
Limiting indices	$-17\leq h\leq 17$, $-15\leq k\leq 15$, $-23\leq l\leq 22$
Reflections collected / unique	25102 / 6520 [R(int) = 0.0197]
Completeness to θ = 30.63	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.97044
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6520 / 0 / 253
Goodness-of-fit on F^2	1.003

Final R indices [I>2σ(I)]	$R_1 = 0.0237$, $wR_2 = 0.0581$
R indices (all data)	$R_1 = 0.0302$, $wR_2 = 0.0593$
Largest diff. peak and hole	0.396 and -0.289 e. $Å^{-3}$

Table A1-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**8**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
C(2)	8881(1)	7848(1)	2555(1)	15(1)
C(4)	8857(1)	9236(1)	3584(1)	19(1)
C(5)	9003(1)	8140(1)	3960(1)	20(1)
C(6)	8715(1)	9851(1)	2028(1)	15(1)
C(7)	8714(1)	9258(1)	1270(1)	14(1)
C(8)	8633(1)	9966(1)	548(1)	15(1)
C(9)	8581(1)	11217(1)	563(1)	18(1)
C(10)	8600(1)	11767(1)	1346(1)	20(1)
C(11)	8663(1)	11097(1)	2090(1)	18(1)
C(13)	8681(1)	8052(1)	-87(1)	14(1)
C(15)	8540(1)	8531(1)	-1467(1)	20(1)
C(16)	8530(1)	9578(1)	-1042(1)	18(1)
C(17)	9199(1)	6015(1)	3495(1)	17(1)
C(18)	10445(1)	5721(1)	3799(1)	22(1)
C(19)	10639(1)	4392(1)	4035(1)	24(1)
C(20)	10299(1)	3552(1)	3269(1)	30(1)
C(21)	8763(1)	6331(1)	-1065(1)	18(1)
C(22)	7786(1)	5849(1)	-1773(1)	22(1)
C(23)	6695(1)	5678(1)	-1511(1)	27(1)
C(24)	6736(1)	4634(1)	-890(1)	35(1)
N(1)	9012(1)	7304(1)	3322(1)	16(1)
N(3)	8790(1)	9041(1)	2724(1)	15(1)
N(12)	8617(1)	9267(1)	-194(1)	15(1)
N(14)	8633(1)	7608(1)	-871(1)	15(1)
Cl(1)	6832(1)	7332(1)	813(1)	20(1)
Cl(2)	10725(1)	7351(1)	1466(1)	21(1)
Cl(3)	8782(1)	5237(1)	1298(1)	23(1)
Ti	8788(1)	7319(1)	1209(1)	12(1)

Table A1-3. Bond lengths [Å] and angles [°] for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**8**).

C(2)-N(1)	1.3474(13)	C(8)-C(7)-Ti	121.53(7)
C(2)-N(3)	1.3647(13)	C(6)-C(7)-Ti	121.64(7)
C(2)-Ti	2.2192(10)	C(7)-C(8)-C(9)	123.13(10)
C(4)-C(5)	1.3520(16)	C(7)-C(8)-N(12)	112.09(9)
C(4)-N(3)	1.3815(13)	C(9)-C(8)-N(12)	124.77(10)
C(5)-N(1)	1.3870(13)	C(10)-C(9)-C(8)	117.57(10)
C(6)-C(7)	1.3861(14)	C(9)-C(10)-C(11)	121.73(10)
C(6)-C(11)	1.3916(14)	C(6)-C(11)-C(10)	117.57(10)
C(6)-N(3)	1.4220(13)	N(14)-C(13)-N(12)	105.03(9)
C(7)-C(8)	1.3864(14)	N(14)-C(13)-Ti	136.79(7)
C(7)-Ti	2.1610(10)	N(12)-C(13)-Ti	118.16(7)
C(8)-C(9)	1.3930(14)	C(16)-C(15)-N(14)	107.22(9)
C(8)-N(12)	1.4215(13)	C(15)-C(16)-N(12)	105.99(9)
C(9)-C(10)	1.3949(16)	N(1)-C(17)-C(18)	111.51(9)
C(10)-C(11)	1.3961(16)	C(17)-C(18)-C(19)	111.51(9)
C(13)-N(14)	1.3422(13)	C(20)-C(19)-C(18)	113.64(10)
C(13)-N(12)	1.3612(13)	N(14)-C(21)-C(22)	112.96(9)
C(13)-Ti	2.2115(10)	C(21)-C(22)-C(23)	114.75(10)
C(15)-C(16)	1.3525(15)	C(22)-C(23)-C(24)	113.41(10)
C(15)-N(14)	1.3891(13)	C(2)-N(1)-C(5)	110.88(9)
C(16)-N(12)	1.3849(13)	C(2)-N(1)-C(17)	125.97(9)
C(17)-N(1)	1.4672(13)	C(5)-N(1)-C(17)	123.08(9)
C(17)-C(18)	1.5179(15)	C(2)-N(3)-C(4)	111.48(9)
C(18)-C(19)	1.5292(16)	C(2)-N(3)-C(6)	116.72(8)
C(19)-C(20)	1.5167(17)	C(4)-N(3)-C(6)	131.67(9)
C(21)-N(14)	1.4720(13)	C(13)-N(12)-C(16)	111.06(9)
C(21)-C(22)	1.5207(15)	C(13)-N(12)-C(8)	116.70(8)
C(22)-C(23)	1.5218(17)	C(16)-N(12)-C(8)	132.23(9)
C(23)-C(24)	1.5247(18)	C(13)-N(14)-C(15)	110.69(9)
Cl(1)-Ti	2.3237(3)	C(13)-N(14)-C(21)	125.02(9)
Cl(2)-Ti	2.3119(3)	C(15)-N(14)-C(21)	124.08(9)
Cl(3)-Ti	2.3198(3)	C(7)-Ti-C(13)	71.52(4)
		C(7)-Ti-C(2)	71.51(4)
N(1)-C(2)-N(3)	104.42(8)	C(13)-Ti-C(2)	143.01(4)
N(1)-C(2)-Ti	137.75(7)	C(7)-Ti-Cl(2)	91.75(3)
N(3)-C(2)-Ti	117.83(7)	C(13)-Ti-Cl(2)	88.14(3)
C(5)-C(4)-N(3)	105.90(9)	C(2)-Ti-Cl(2)	91.91(3)
C(4)-C(5)-N(1)	107.31(9)	C(7)-Ti-Cl(3)	172.70(3)
C(7)-C(6)-C(11)	123.18(10)	C(13)-Ti-Cl(3)	115.20(3)
C(7)-C(6)-N(3)	112.17(9)	C(2)-Ti-Cl(3)	101.78(3)
C(11)-C(6)-N(3)	124.65(10)	Cl(2)-Ti-Cl(3)	91.344(11)
C(8)-C(7)-C(6)	116.81(9)	C(7)-Ti-Cl(1)	87.34(3)

C(13)-Ti-Cl(1)	86.43(3)	Cl(2)-Ti-Cl(1)	174.506(13)
C(2)-Ti-Cl(1)	92.94(3)	Cl(3)-Ti-Cl(1)	90.199(11)

Table A1-4. Anisotropic displacement parameters ($Å^2$ x 10^3) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**8**). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

Atom	U11	U22	U33	U23	U13	U12
C(2)	15(1)	14(1)	15(1)	-1(1)	4(1)	1(1)
C(4)	21(1)	19(1)	17(1)	-4(1)	7(1)	2(1)
C(5)	25(1)	22(1)	14(1)	-3(1)	7(1)	1(1)
C(6)	14(1)	13(1)	17(1)	0(1)	4(1)	1(1)
C(7)	15(1)	12(1)	16(1)	0(1)	4(1)	1(1)
C(8)	14(1)	13(1)	17(1)	0(1)	3(1)	0(1)
C(9)	17(1)	13(1)	23(1)	3(1)	4(1)	0(1)
C(10)	19(1)	11(1)	29(1)	-1(1)	5(1)	0(1)
C(11)	18(1)	13(1)	22(1)	-4(1)	5(1)	0(1)
C(13)	14(1)	14(1)	15(1)	1(1)	4(1)	0(1)
C(15)	22(1)	23(1)	15(1)	5(1)	5(1)	1(1)
C(16)	20(1)	19(1)	16(1)	6(1)	5(1)	0(1)
C(17)	19(1)	15(1)	16(1)	2(1)	5(1)	0(1)
C(18)	18(1)	18(1)	26(1)	0(1)	2(1)	0(1)
C(19)	21(1)	21(1)	25(1)	4(1)	0(1)	3(1)
C(20)	41(1)	21(1)	31(1)	-1(1)	14(1)	4(1)
C(21)	20(1)	17(1)	18(1)	-1(1)	5(1)	4(1)
C(22)	24(1)	22(1)	19(1)	-4(1)	4(1)	0(1)
C(23)	21(1)	28(1)	32(1)	0(1)	5(1)	-1(1)
C(24)	31(1)	35(1)	38(1)	4(1)	7(1)	-9(1)
N(1)	18(1)	15(1)	14(1)	-1(1)	5(1)	1(1)
N(3)	17(1)	14(1)	15(1)	-2(1)	5(1)	2(1)
N(12)	17(1)	13(1)	15(1)	2(1)	4(1)	0(1)
N(14)	16(1)	16(1)	14(1)	1(1)	4(1)	1(1)
Cl(1)	15(1)	20(1)	25(1)	6(1)	5(1)	1(1)
Cl(2)	16(1)	20(1)	28(1)	3(1)	6(1)	1(1)
Cl(3)	24(1)	11(1)	32(1)	1(1)	6(1)	1(1)
Ti	15(1)	10(1)	12(1)	0(1)	4(1)	1(1)

Table A1-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) titanium(IV) (**8**).

Atom	x	y	z	U(eq)
H(4)	8810	9986	3854	23
H(5)	9085	7973	4552	24
H(9)	8534	11679	58	22
H(10)	8570	12619	1373	24
H(11)	8669	11477	2619	21
H(15)	8493	8443	-2063	24
H(16)	8474	10366	-1277	22
H(17A)	8859	5555	2964	20
H(17B)	8822	5765	3940	20
H(18A)	10795	6221	4307	26
H(18B)	10812	5921	3338	26
H(19A)	11446	4268	4322	28
H(19B)	10205	4180	4453	28
H(20A)	9492	3640	2997	36
H(20B)	10459	2720	3463	36
H(20C)	10726	3752	2852	36
H(21A)	8827	5852	-536	22
H(21B)	9469	6227	-1242	22
H(22A)	8010	5067	-1971	26
H(22B)	7645	6411	-2267	26
H(23A)	6075	5536	-2035	33
H(23B)	6522	6427	-1239	33
H(24A)	6937	3894	-1144	42
H(24B)	5996	4537	-776	42
H(24C)	7301	4801	-348	42

Table A1-6. Torsion angles [°] for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)trichloro titanium(IV) (**8**).

N(3)-C(4)-C(5)-N(1)	-0.53(12)	Ti-C(13)-N(12)-C(8)	0.41(12)
C(11)-C(6)-C(7)-C(8)	-1.24(15)	C(15)-C(16)-N(12)-C(13)	-0.04(12)
N(3)-C(6)-C(7)-C(8)	179.45(9)	C(15)-C(16)-N(12)-C(8)	-178.89(10)
C(11)-C(6)-C(7)-Ti	-179.65(8)	C(7)-C(8)-N(12)-C(13)	0.03(13)
N(3)-C(6)-C(7)-Ti	1.04(12)	C(9)-C(8)-N(12)-C(13)	179.68(10)
C(6)-C(7)-C(8)-C(9)	1.45(15)	C(7)-C(8)-N(12)-C(16)	178.83(10)
Ti-C(7)-C(8)-C(9)	179.86(8)	C(9)-C(8)-N(12)-C(16)	-1.53(18)
C(6)-C(7)-C(8)-N(12)	-178.90(9)	N(12)-C(13)-N(14)-C(15)	0.02(11)
Ti-C(7)-C(8)-N(12)	-0.49(12)	Ti-C(13)-N(14)-C(15)	178.28(8)
C(7)-C(8)-C(9)-C(10)	-0.68(16)	N(12)-C(13)-N(14)-C(21)	174.86(9)
N(12)-C(8)-C(9)-C(10)	179.71(10)	Ti-C(13)-N(14)-C(21)	-6.88(16)
C(8)-C(9)-C(10)-C(11)	-0.35(16)	C(16)-C(15)-N(14)-C(13)	-0.05(12)
C(7)-C(6)-C(11)-C(10)	0.29(16)	C(16)-C(15)-N(14)-C(21)	-174.94(9)
N(3)-C(6)-C(11)-C(10)	179.51(9)	C(22)-C(21)-N(14)-C(13)	125.90(11)
C(9)-C(10)-C(11)-C(6)	0.54(16)	C(22)-C(21)-N(14)-C(15)	-59.94(13)
N(14)-C(15)-C(16)-N(12)	0.05(12)	C(8)-C(7)-Ti-C(13)	0.52(8)
N(1)-C(17)-C(18)-C(19)	176.23(9)	C(6)-C(7)-Ti-C(13)	178.86(9)
C(17)-C(18)-C(19)-C(20)	68.14(13)	C(8)-C(7)-Ti-C(2)	179.40(9)
N(14)-C(21)-C(22)-C(23)	-72.35(12)	C(6)-C(7)-Ti-C(2)	-2.27(8)
C(21)-C(22)-C(23)-C(24)	-70.76(14)	C(8)-C(7)-Ti-Cl(2)	87.97(8)
N(3)-C(2)-N(1)-C(5)	-0.02(12)	C(6)-C(7)-Ti-Cl(2)	-93.69(8)
Ti-C(2)-N(1)-C(5)	179.97(9)	C(8)-C(7)-Ti-Cl(3)	-156.98(18)
N(3)-C(2)-N(1)-C(17)	-176.98(9)	C(6)-C(7)-Ti-Cl(3)	21.4(3)
Ti-C(2)-N(1)-C(17)	3.01(17)	C(8)-C(7)-Ti-Cl(1)	-86.60(8)
C(4)-C(5)-N(1)-C(2)	0.36(13)	C(6)-C(7)-Ti-Cl(1)	91.73(8)
C(4)-C(5)-N(1)-C(17)	177.42(9)	N(14)-C(13)-Ti-C(7)	-178.57(11)
C(18)-C(17)-N(1)-C(2)	93.43(12)	N(12)-C(13)-Ti-C(7)	-0.48(7)
C(18)-C(17)-N(1)-C(5)	-83.18(12)	N(14)-C(13)-Ti-C(2)	179.65(9)
N(1)-C(2)-N(3)-C(4)	-0.33(11)	N(12)-C(13)-Ti-C(2)	-2.26(11)
Ti-C(2)-N(3)-C(4)	179.68(7)	N(14)-C(13)-Ti-Cl(2)	88.96(10)
N(1)-C(2)-N(3)-C(6)	176.07(8)	N(12)-C(13)-Ti-Cl(2)	-92.95(7)
Ti-C(2)-N(3)-C(6)	-3.92(12)	N(14)-C(13)-Ti-Cl(3)	-1.65(12)
C(5)-C(4)-N(3)-C(2)	0.55(12)	N(12)-C(13)-Ti-Cl(3)	176.44(7)
C(5)-C(4)-N(3)-C(6)	-175.15(10)	N(14)-C(13)-Ti-Cl(1)	-90.19(10)
C(7)-C(6)-N(3)-C(2)	1.91(13)	N(12)-C(13)-Ti-Cl(1)	87.90(7)
C(11)-C(6)-N(3)-C(2)	-177.39(10)	N(1)-C(2)-Ti-C(7)	-176.76(12)
C(7)-C(6)-N(3)-C(4)	177.42(10)	N(3)-C(2)-Ti-C(7)	3.23(7)
C(11)-C(6)-N(3)-C(4)	-1.87(17)	N(1)-C(2)-Ti-C(13)	-174.98(9)
N(14)-C(13)-N(12)-C(16)	0.01(11)	N(3)-C(2)-Ti-C(13)	5.01(11)
Ti-C(13)-N(12)-C(16)	-178.63(7)	N(1)-C(2)-Ti-Cl(2)	-85.55(11)
N(14)-C(13)-N(12)-C(8)	179.06(8)	N(3)-C(2)-Ti-Cl(2)	94.44(7)

N(1)-C(2)-Ti-Cl(3)	6.22(11)	N(1)-C(2)-Ti-Cl(1)	97.04(11)
N(3)-C(2)-Ti-Cl(3)	-173.78(7)	N(3)-C(2)-Ti-Cl(1)	-82.97(7)

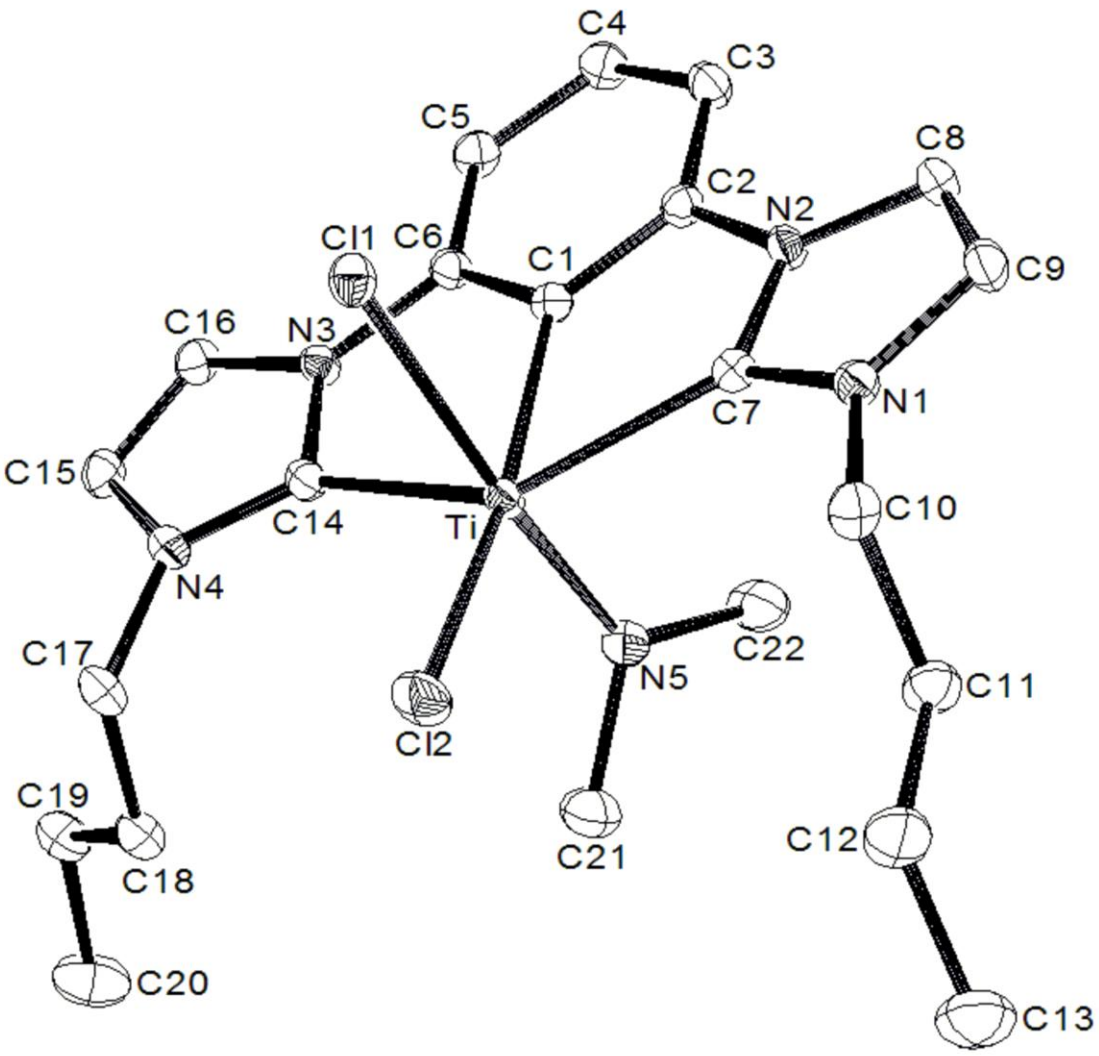


Figure A2. 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (**11**).

Table A2-1. Crystal data and structure refinement for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) titanium(IV) (**11**).

Empirical formula	$C_{22}H_{31}N_5TiCl_2$
Formula weight	484.32
Temperature	101(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P^2(1)/n$
Unit cell dimensions	a = 11.8116(3) Å $\alpha = 90^o$. b = 13.0347(3) Å $\beta = 93.963(2)^o$. c = 15.5092(3) Å $\gamma = 90^o$.
Volume	2382.10(9) $Å^3$
Z, Calculated density	4, 1.354 Mg/m^3
Absorption coefficient	0.604 mm^{-1}
F(000)	1016
Crystal size	0.46 x 0.31 x 0.09 mm
θ range for data collection	3.39 to 30.57°.
Limiting indices	$-16\leq h\leq 13$, $-18\leq k\leq 18$, $-22\leq l\leq 21$
Reflections collected / unique	14249 / 7288 [R(int) = 0.0287]
Completeness to θ = 30.57	99.9 %
Absorption correction	Analytical
Max. and min. transmission	0.9231 and 0.6814
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7288 / 0 / 271
Goodness-of-fit on F^2	0.955
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0635$

R indices (all data)	$R_1 = 0.0548$, $wR_2 = 0.0658$
Largest diff. peak and hole	0.401 and -0.351 e.Å^{-3}

Table A2-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å ^{2} x 10^3) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (**11**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
C(1)	3783(1)	9326(1)	1940(1)	13(1)
C(2)	4414(1)	8782(1)	2568(1)	14(1)
C(3)	5036(1)	9234(1)	3256(1)	17(1)
C(4)	5027(1)	10301(1)	3302(1)	19(1)
C(5)	4402(1)	10892(1)	2697(1)	17(1)
C(6)	3780(1)	10384(1)	2035(1)	14(1)
C(7)	3602(1)	7383(1)	1761(1)	14(1)
C(8)	4817(1)	6875(1)	2874(1)	16(1)
C(9)	4378(1)	6029(1)	2484(1)	17(1)
C(10)	2966(1)	5670(1)	1221(1)	17(1)
C(11)	3543(1)	5416(1)	404(1)	19(1)
C(12)	2732(1)	4873(1)	-247(1)	25(1)
C(13)	3265(2)	4583(1)	-1078(1)	30(1)
C(14)	2494(1)	10267(1)	785(1)	14(1)
C(15)	1995(1)	11924(1)	596(1)	17(1)
C(16)	2753(1)	11894(1)	1286(1)	16(1)
C(17)	1145(1)	10643(1)	-482(1)	17(1)
C(18)	1720(1)	10831(1)	-1312(1)	19(1)
C(19)	1911(1)	11956(1)	-1520(1)	21(1)
C(20)	2376(2)	12091(1)	-2402(1)	34(1)
C(21)	3855(1)	8571(1)	-771(1)	28(1)
C(22)	5211(1)	8466(1)	426(1)	28(1)
N(1)	3634(1)	6351(1)	1807(1)	14(1)
N(2)	4328(1)	7698(1)	2425(1)	14(1)
N(3)	3054(1)	10874(1)	1391(1)	13(1)
N(4)	1854(1)	10926(1)	297(1)	15(1)
N(5)	4003(1)	8531(1)	173(1)	18(1)
Cl(1)	1294(1)	8571(1)	1956(1)	16(1)
Cl(2)	1440(1)	7742(1)	-61(1)	22(1)
Ti	2780(1)	8572(1)	909(1)	13(1)

Table A2-3. Bond lengths [Å] and angles [°] for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (**11**).

C(1)-C(2)	1.3807(19)	C(4)-C(5)-C(6)	117.73(12)
C(1)-C(6)	1.3869(19)	C(1)-C(6)-C(5)	123.20(13)
C(1)-Ti	2.1593(14)	C(1)-C(6)-N(3)	112.19(12)
C(2)-C(3)	1.3851(19)	C(5)-C(6)-N(3)	124.59(12)
C(2)-N(2)	1.4316(17)	N(1)-C(7)-N(2)	104.38(12)
C(3)-C(4)	1.3935(19)	N(1)-C(7)-Ti	137.67(10)
C(4)-C(5)	1.386(2)	N(2)-C(7)-Ti	117.89(9)
C(5)-C(6)	1.3883(19)	C(9)-C(8)-N(2)	105.95(12)
C(6)-N(3)	1.4213(17)	C(8)-C(9)-N(1)	107.34(12)
C(7)-N(1)	1.3475(17)	N(1)-C(10)-C(11)	113.44(12)
C(7)-N(2)	1.3579(17)	C(10)-C(11)-C(12)	111.00(12)
C(7)-Ti	2.2172(14)	C(11)-C(12)-C(13)	113.59(13)
C(8)-C(9)	1.344(2)	N(4)-C(14)-N(3)	104.18(11)
C(8)-N(2)	1.3833(17)	N(4)-C(14)-Ti	139.01(10)
C(9)-N(1)	1.3857(18)	N(3)-C(14)-Ti	116.68(9)
C(10)-N(1)	1.4618(18)	C(16)-C(15)-N(4)	107.25(12)
C(10)-C(11)	1.516(2)	C(15)-C(16)-N(3)	105.77(12)
C(11)-C(12)	1.518(2)	N(4)-C(17)-C(18)	113.19(12)
C(12)-C(13)	1.520(2)	C(17)-C(18)-C(19)	114.72(12)
C(14)-N(4)	1.3424(17)	C(20)-C(19)-C(18)	111.81(13)
C(14)-N(3)	1.3646(17)	C(7)-N(1)-C(9)	110.84(12)
C(14)-Ti	2.2406(14)	C(7)-N(1)-C(10)	124.10(12)
C(15)-C(16)	1.348(2)	C(9)-N(1)-C(10)	125.06(12)
C(15)-N(4)	1.3869(17)	C(7)-N(2)-C(8)	111.49(11)
C(16)-N(3)	1.3841(17)	C(7)-N(2)-C(2)	116.74(11)
C(17)-N(4)	1.4684(18)	C(8)-N(2)-C(2)	131.69(12)
C(17)-C(18)	1.516(2)	C(14)-N(3)-C(16)	111.57(12)
C(18)-C(19)	1.522(2)	C(14)-N(3)-C(6)	117.65(11)
C(19)-C(20)	1.519(2)	C(16)-N(3)-C(6)	130.69(12)
C(21)-N(5)	1.4628(18)	C(14)-N(4)-C(15)	111.22(12)
C(22)-N(5)	1.4560(19)	C(14)-N(4)-C(17)	124.74(11)
N(5)-Ti	1.9032(12)	C(15)-N(4)-C(17)	123.96(12)
Cl(1)-Ti	2.4725(4)	C(22)-N(5)-C(21)	108.62(12)
Cl(2)-Ti	2.3686(4)	C(22)-N(5)-Ti	127.60(10)
C(2)-C(1)-C(6)	116.21(13)	C(21)-N(5)-Ti	123.78(10)
C(2)-C(1)-Ti	121.99(10)	N(5)-Ti-C(1)	93.26(5)
C(6)-C(1)-Ti	121.72(10)	N(5)-Ti-C(7)	91.09(5)
C(1)-C(2)-C(3)	123.79(12)	C(1)-Ti-C(7)	71.44(5)
C(1)-C(2)-N(2)	111.68(12)	N(5)-Ti-C(14)	95.30(5)
C(3)-C(2)-N(2)	124.52(12)	C(1)-Ti-C(14)	71.76(5)
C(2)-C(3)-C(4)	117.31(13)	C(7)-Ti-C(14)	142.93(5)
C(5)-C(4)-C(3)	121.71(14)	N(5)-Ti-Cl(2)	96.19(4)

C(1)-Ti-Cl(2)	170.53(4)	C(1)-Ti-Cl(1)	83.80(4)
C(7)-Ti-Cl(2)	107.73(4)	C(7)-Ti-Cl(1)	84.79(4)
C(14)-Ti-Cl(2)	107.80(4)	C(14)-Ti-Cl(1)	86.99(4)
N(5)-Ti-Cl(1)	175.54(4)	Cl(2)-Ti-Cl(1)	86.725(15)

Table A2-4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (**11**). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

Atom	U11	U22	U33	U23	U13	U12
C(1)	13(1)	14(1)	13(1)	0(1)	1(1)	0(1)
C(2)	14(1)	12(1)	14(1)	-2(1)	1(1)	0(1)
C(3)	19(1)	17(1)	16(1)	0(1)	-4(1)	2(1)
C(4)	18(1)	20(1)	18(1)	-5(1)	-4(1)	-2(1)
C(5)	18(1)	14(1)	19(1)	-3(1)	0(1)	-2(1)
C(6)	14(1)	15(1)	13(1)	1(1)	1(1)	0(1)
C(7)	14(1)	13(1)	13(1)	-1(1)	1(1)	1(1)
C(8)	17(1)	17(1)	14(1)	3(1)	-1(1)	4(1)
C(9)	17(1)	16(1)	17(1)	4(1)	0(1)	3(1)
C(10)	16(1)	13(1)	21(1)	-1(1)	0(1)	-2(1)
C(11)	19(1)	20(1)	19(1)	-4(1)	0(1)	-1(1)
C(12)	24(1)	25(1)	25(1)	-8(1)	-4(1)	-1(1)
C(13)	34(1)	33(1)	23(1)	-9(1)	-2(1)	-3(1)
C(14)	13(1)	16(1)	13(1)	2(1)	1(1)	0(1)
C(15)	20(1)	13(1)	19(1)	3(1)	4(1)	3(1)
C(16)	21(1)	10(1)	18(1)	0(1)	3(1)	1(1)
C(17)	17(1)	17(1)	18(1)	3(1)	-5(1)	-1(1)
C(18)	19(1)	20(1)	18(1)	1(1)	-3(1)	-1(1)
C(19)	22(1)	24(1)	19(1)	4(1)	-2(1)	-3(1)
C(20)	47(1)	35(1)	21(1)	7(1)	3(1)	-12(1)
C(21)	27(1)	39(1)	17(1)	2(1)	2(1)	4(1)
C(22)	18(1)	45(1)	20(1)	0(1)	4(1)	1(1)
N(1)	15(1)	13(1)	14(1)	0(1)	0(1)	0(1)
N(2)	15(1)	11(1)	14(1)	1(1)	-2(1)	2(1)
N(3)	16(1)	11(1)	13(1)	1(1)	0(1)	0(1)
N(4)	14(1)	15(1)	14(1)	2(1)	-1(1)	0(1)
N(5)	18(1)	18(1)	16(1)	-2(1)	0(1)	1(1)
Cl(1)	16(1)	14(1)	19(1)	2(1)	1(1)	0(1)
Cl(2)	22(1)	24(1)	20(1)	-5(1)	-8(1)	-1(1)
Ti	14(1)	12(1)	12(1)	0(1)	-3(1)	0(1)

Table A2-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å ^{2} x 10^3) for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (**11**).

Atom	x	y	z	U(eq)
H(3)	5453	8832	3679	21
H(4)	5459	10633	3760	23
H(5)	4399	11619	2734	20
H(8)	5354	6902	3359	19
H(9)	4546	5339	2642	20
H(10A)	2226	5999	1059	20
H(10B)	2814	5025	1528	20
H(11A)	4208	4971	550	23
H(11B)	3817	6056	145	23
H(12A)	2072	5325	-391	30
H(12B)	2448	4243	22	30
H(13A)	3581	5197	-1335	36
H(13B)	2686	4282	-1485	36
H(13C)	3872	4082	-949	36
H(15)	1626	12517	358	21
H(16)	3025	12458	1629	20
H(17A)	431	11042	-497	21
H(17B)	944	9907	-448	21
H(18A)	1251	10518	-1796	23
H(18B)	2463	10477	-1272	23
H(19A)	1183	12331	-1507	26
H(19B)	2450	12256	-1073	26
H(20A)	3049	11659	-2440	41
H(20B)	2582	12811	-2481	41
H(20C)	1796	11891	-2853	41
H(21A)	4248	9174	-981	33
H(21B)	3044	8617	-950	33
H(21C)	4172	7949	-1014	33
H(22A)	5523	7839	186	33
H(22B)	5324	8451	1058	33
H(22C)	5600	9065	204	33

Table A2-6. Torsion angles [°] for 2-(1,3-bis(3-butylimidazol-1-yl-2-idene)phenylene)dichloro(dimethylamido) (**11**).

C(6)-C(1)-C(2)-C(3)	-1.0(2)	C(15)-C(16)-N(3)-C(14)	-0.46(16)
Ti-C(1)-C(2)-C(3)	-177.68(11)	C(15)-C(16)-N(3)-C(6)	-176.79(13)
C(6)-C(1)-C(2)-N(2)	178.03(11)	C(1)-C(6)-N(3)-C(14)	-0.90(17)
Ti-C(1)-C(2)-N(2)	1.34(16)	C(5)-C(6)-N(3)-C(14)	-179.58(13)
C(1)-C(2)-C(3)-C(4)	-0.8(2)	C(1)-C(6)-N(3)-C(16)	175.25(13)
N(2)-C(2)-C(3)-C(4)	-179.69(13)	C(5)-C(6)-N(3)-C(16)	-3.4(2)
C(2)-C(3)-C(4)-C(5)	1.4(2)	N(3)-C(14)-N(4)-C(15)	-0.86(15)
C(3)-C(4)-C(5)-C(6)	-0.1(2)	Ti-C(14)-N(4)-C(15)	174.55(12)
C(2)-C(1)-C(6)-C(5)	2.4(2)	N(3)-C(14)-N(4)-C(17)	175.93(12)
Ti-C(1)-C(6)-C(5)	179.05(11)	Ti-C(14)-N(4)-C(17)	-8.7(2)
C(2)-C(1)-C(6)-N(3)	-176.34(12)	C(16)-C(15)-N(4)-C(14)	0.62(16)
Ti-C(1)-C(6)-N(3)	0.35(16)	C(16)-C(15)-N(4)-C(17)	-176.21(12)
C(4)-C(5)-C(6)-C(1)	-1.8(2)	C(18)-C(17)-N(4)-C(14)	-96.88(16)
C(4)-C(5)-C(6)-N(3)	176.70(13)	C(18)-C(17)-N(4)-C(15)	79.51(17)
N(2)-C(8)-C(9)-N(1)	0.09(15)	C(22)-N(5)-Ti-C(1)	30.00(13)
N(1)-C(10)-C(11)-C(12)	-169.73(12)	C(21)-N(5)-Ti-C(1)	-149.48(12)
C(10)-C(11)-C(12)-C(13)	-179.19(13)	C(22)-N(5)-Ti-C(7)	-41.48(13)
N(4)-C(15)-C(16)-N(3)	-0.09(16)	C(21)-N(5)-Ti-C(7)	139.05(12)
N(4)-C(17)-C(18)-C(19)	-67.72(17)	C(22)-N(5)-Ti-C(14)	101.96(13)
C(17)-C(18)-C(19)-C(20)	-174.10(14)	C(21)-N(5)-Ti-C(14)	-77.51(12)
N(2)-C(7)-N(1)-C(9)	-0.59(15)	C(22)-N(5)-Ti-Cl(2)	-149.44(12)
Ti-C(7)-N(1)-C(9)	176.36(11)	C(21)-N(5)-Ti-Cl(2)	31.08(12)
N(2)-C(7)-N(1)-C(10)	179.09(12)	C(22)-N(5)-Ti-Cl(1)	-18.8(6)
Ti-C(7)-N(1)-C(10)	-4.0(2)	C(21)-N(5)-Ti-Cl(1)	161.8(4)
C(8)-C(9)-N(1)-C(7)	0.32(16)	C(2)-C(1)-Ti-N(5)	-88.86(12)
C(8)-C(9)-N(1)-C(10)	-179.35(12)	C(6)-C(1)-Ti-N(5)	94.63(11)
C(11)-C(10)-N(1)-C(7)	87.30(16)	C(2)-C(1)-Ti-C(7)	1.20(11)
C(11)-C(10)-N(1)-C(9)	-93.06(16)	C(6)-C(1)-Ti-C(7)	-175.31(12)
N(1)-C(7)-N(2)-C(8)	0.65(15)	C(2)-C(1)-Ti-C(14)	176.63(12)
Ti-C(7)-N(2)-C(8)	-177.03(9)	C(6)-C(1)-Ti-C(14)	0.12(11)
N(1)-C(7)-N(2)-C(2)	-176.37(11)	C(2)-C(1)-Ti-Cl(2)	87.8(3)
Ti-C(7)-N(2)-C(2)	5.95(15)	C(6)-C(1)-Ti-Cl(2)	-88.7(3)
C(9)-C(8)-N(2)-C(7)	-0.47(15)	C(2)-C(1)-Ti-Cl(1)	87.76(11)
C(9)-C(8)-N(2)-C(2)	175.96(13)	C(6)-C(1)-Ti-Cl(1)	-88.74(11)
C(1)-C(2)-N(2)-C(7)	-4.67(17)	N(1)-C(7)-Ti-N(5)	-87.39(15)
C(3)-C(2)-N(2)-C(7)	174.34(13)	N(2)-C(7)-Ti-N(5)	89.27(11)
C(1)-C(2)-N(2)-C(8)	179.05(13)	N(1)-C(7)-Ti-C(1)	179.54(16)
C(3)-C(2)-N(2)-C(8)	-1.9(2)	N(2)-C(7)-Ti-C(1)	-3.80(10)
N(4)-C(14)-N(3)-C(16)	0.81(15)	N(1)-C(7)-Ti-C(14)	172.33(12)
Ti-C(14)-N(3)-C(16)	-175.82(9)	N(2)-C(7)-Ti-C(14)	-11.01(15)
N(4)-C(14)-N(3)-C(6)	177.67(11)	N(1)-C(7)-Ti-Cl(2)	9.47(15)
Ti-C(14)-N(3)-C(6)	1.04(15)	N(2)-C(7)-Ti-Cl(2)	-173.87(9)

N(1)-C(7)-Ti-Cl(1)	94.34(14)	N(4)-C(14)-Ti-C(7)	-168.43(13)
N(2)-C(7)-Ti-Cl(1)	-89.00(10)	N(3)-C(14)-Ti-C(7)	6.59(15)
N(4)-C(14)-Ti-N(5)	92.68(15)	N(4)-C(14)-Ti-Cl(2)	-5.58(16)
N(3)-C(14)-Ti-N(5)	-92.31(10)	N(3)-C(14)-Ti-Cl(2)	169.44(9)
N(4)-C(14)-Ti-C(1)	-175.63(16)	N(4)-C(14)-Ti-Cl(1)	-91.16(15)
N(3)-C(14)-Ti-C(1)	-0.61(9)	N(3)-C(14)-Ti-Cl(1)	83.85(10)

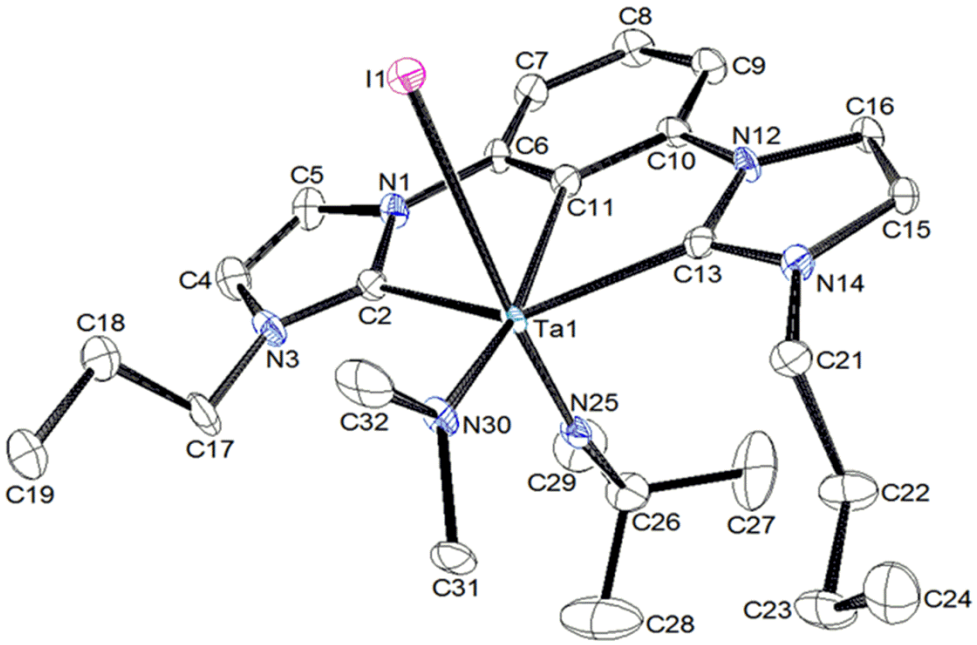


Figure A3. (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).

Table A3-1. Crystal data and structure refinement (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).

Empirical formula	$C_{26}H_{40}N_6ITa$
Formula weight	744.49
Temperature/K	100.15
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.3134(5)
b/Å	14.0461(5)
c/Å	14.6772(5)
α/°	90
β/°	95.1620(10)
γ/°	90
Volume/Å^3	2938.85(18)
Z	4
ρ_{calc}mg/mm^3	1.683
m/mm^{-1}	15.326
F(000)	1456.0
Crystal size/mm^3	0.2 × 0.15 × 0.15
2Θ range for data collection	6.2 to 139.862°
Index ranges	$-13 \leq h \leq 17$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$
Reflections collected	27074
Independent reflections	5465[R(int) = 0.0508]
Data/restraints/parameters	5465/0/314
Goodness-of-fit on F^2	1.106
Final R indexes [I>=2σ (I)]	$R_1 = 0.0491$, $wR_2 = 0.1362$
Final R indexes [all data]	$R_1 = 0.0497$, $wR_2 = 0.1370$

Table A3-2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*Y*	*Z*	U(eq)
Ta1	2200.8(2)	742.0(2)	3457.3(2)	10.71(13)
I1	2656.0(2)	1197.6(2)	5492.4(2)	15.07(14)
N1	4366(3)	252(3)	3718(3)	14.5(9)
C2	3760(4)	976(4)	3447(4)	14.1(10)
N3	4323(4)	1672(3)	3171(3)	18.4(10)
C4	5261(4)	1395(5)	3288(5)	23.9(12)
C5	5287(4)	517(5)	3629(4)	19.9(11)
C6	3969(4)	-617(4)	4007(4)	14.2(11)
C7	4473(4)	-1444(4)	4235(4)	18.5(11)
C8	3973(4)	-2242(4)	4484(4)	21.5(12)
C9	2990(4)	-2218(4)	4489(4)	19.2(11)
C10	2540(4)	-1369(4)	4253(4)	14.9(10)
C11	2994(4)	-549(4)	4003(4)	13.9(10)
N12	1547(3)	-1217(3)	4220(3)	13.9(9)
C13	1204(4)	-353(4)	3939(4)	13.1(10)
N14	257(3)	-438(3)	3961(3)	13.9(9)
C15	17(4)	-1336(4)	4240(4)	15.1(11)
C16	825(4)	-1832(4)	4402(4)	15.7(11)
C17	3983(5)	2605(4)	2856(4)	23.5(13)
C18	4124(5)	3353(4)	3609(5)	25.8(13)
C19	3706(6)	4305(4)	3300(5)	31.2(16)
C20	3927(7)	5105(6)	3961(6)	46(2)
C21	-414(4)	327(4)	3676(4)	15.5(11)
C22	-826(5)	199(5)	2690(4)	23.9(13)
C23	-1407(5)	1059(5)	2338(5)	27.7(14)
C24	-2217(5)	1295(5)	2892(5)	28.1(14)
N25	2084(4)	290(3)	2310(3)	17.3(10)
C26	2127(5)	-260(5)	1493(4)	26.5(14)
C27	1481(7)	-1119(6)	1538(7)	54(3)
C28	1854(9)	357(7)	657(5)	57(3)
C29	3144(6)	-612(6)	1471(6)	38.3(17)
N30	1528(3)	2018(3)	3329(3)	16.0(9)
C31	1116(5)	2328(4)	2423(4)	21.1(12)

C32	1333(5)	2774(4)	3961(5)	28.3(14)

Table A3-3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (1,3-bis(3-butyimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (13). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ta1	15.92(18)	2.51(18)	13.50(19)	1.14(7)	0.30(11)	1.64(7)
I1	17.1(2)	13.1(2)	14.7(2)	-1.55(11)	-0.13(14)	3.07(11)
N1	17(2)	7(2)	19(2)	-1.9(17)	2.0(18)	2.7(17)
C2	16(3)	8(2)	17(3)	0(2)	-1(2)	3(2)
N3	24(2)	10(2)	21(2)	3.5(18)	3.9(19)	0.5(18)
C4	22(3)	22(3)	29(3)	1(3)	7(2)	-5(2)
C5	18(3)	18(3)	25(3)	-6(2)	7(2)	-1(2)
C6	21(3)	5(2)	17(3)	-3.3(19)	1(2)	0(2)
C7	18(3)	11(3)	25(3)	-1(2)	-2(2)	5(2)
C8	28(3)	10(3)	26(3)	0(2)	-1(2)	10(2)
C9	26(3)	9(2)	22(3)	2(2)	1(2)	2(2)
C10	22(3)	7(2)	15(2)	1.3(19)	0(2)	3(2)
C11	17(3)	8(2)	17(3)	-1(2)	-1(2)	2(2)
N12	16(2)	7(2)	18(2)	2.4(16)	2.5(18)	-1.7(16)
C13	16(2)	11(2)	12(2)	-2.2(19)	-0.4(19)	0(2)
N14	17(2)	7(2)	17(2)	-1.4(17)	-0.6(17)	0.5(17)
C15	20(3)	9(2)	16(3)	-1(2)	-1(2)	-5(2)
C16	27(3)	3(2)	17(3)	-1.2(19)	0(2)	-3(2)
C17	29(3)	11(3)	31(3)	7(2)	4(3)	-4(2)
C18	32(3)	16(3)	28(3)	-1(2)	-1(3)	-1(2)
C19	43(4)	14(3)	36(4)	2(3)	-4(3)	-3(3)
C20	70(6)	21(4)	45(4)	-5(3)	-7(4)	12(4)
C21	19(3)	9(2)	18(3)	0(2)	-2(2)	4(2)
C22	31(3)	20(3)	20(3)	0(2)	-1(2)	12(2)
C23	34(3)	22(3)	26(3)	10(3)	-3(3)	9(3)
C24	26(3)	19(3)	40(4)	1(3)	2(3)	4(2)
N25	30(3)	7(2)	14(2)	-0.7(17)	-1.0(19)	-3.4(18)
C26	44(4)	19(3)	15(3)	-7(2)	1(3)	0(3)
C27	61(5)	35(5)	66(6)	-38(4)	14(5)	-18(4)
C28	100(8)	50(5)	21(4)	-3(4)	-2(4)	31(5)
C29	41(4)	45(4)	30(4)	-12(3)	14(3)	3(3)
N30	21(2)	4.4(19)	22(2)	1.1(18)	0.6(18)	3.7(17)

C31	30(3)	12(3)	20(3)	5(2)	-4(2)	5(2)
C32	46(4)	11(3)	28(3)	2(2)	3(3)	13(3)

Table A3-4. Bond Lengths for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ta1	I1	3.0669(4)	C10	N12	1.434(7)
Ta1	C2	2.258(6)	N12	C13	1.359(7)
Ta1	C11	2.248(5)	N12	C16	1.391(7)
Ta1	C13	2.255(5)	C13	N14	1.365(7)
Ta1	N25	1.794(5)	N14	C15	1.378(7)
Ta1	N30	2.036(4)	N14	C21	1.476(7)
N1	C2	1.371(7)	C15	C16	1.353(8)
N1	C5	1.387(8)	C17	C18	1.524(9)
N1	C6	1.428(7)	C18	C19	1.519(9)
C2	N3	1.351(8)	C19	C20	1.500(10)
N3	C4	1.394(8)	C21	C22	1.523(8)
N3	C17	1.459(7)	C22	C23	1.530(8)
C4	C5	1.331(9)	C23	C24	1.511(10)
C6	C7	1.393(8)	N25	C26	1.432(8)
C6	C11	1.398(8)	C26	C27	1.524(11)
C7	C8	1.397(9)	C26	C28	1.525(10)
C8	C9	1.407(9)	C26	C29	1.540(11)
C9	C10	1.385(8)	N30	C31	1.472(7)
C10	C11	1.388(8)	N30	C32	1.452(8)

Table A3-5. Bond Angles for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	Ta1	I1	81.53(14)	C9	C10	N12	125.0(5)
C11	Ta1	I1	76.42(14)	C11	C10	N12	110.8(5)
C11	Ta1	C2	69.6(2)	C6	C11	Ta1	121.9(4)
C11	Ta1	C13	69.6(2)	C10	C11	Ta1	122.0(4)
C13	Ta1	I1	85.52(13)	C10	C11	C6	115.6(5)
C13	Ta1	C2	139.1(2)	C13	N12	C10	118.2(4)
N25	Ta1	I1	169.14(16)	C13	N12	C16	111.1(5)
N25	Ta1	C2	93.1(2)	C16	N12	C10	130.7(5)
N25	Ta1	C11	92.9(2)	N12	C13	Ta1	118.9(4)

N25	Ta1	C13	92.6(2)	N12	C13	N14	104.3(5)
N25	Ta1	N30	102.8(2)	N14	C13	Ta1	136.5(4)
N30	Ta1	I1	87.91(14)	C13	N14	C15	111.1(5)
N30	Ta1	C2	109.3(2)	C13	N14	C21	123.5(5)
N30	Ta1	C11	164.3(2)	C15	N14	C21	125.3(5)
N30	Ta1	C13	108.80(19)	C16	C15	N14	107.0(5)
C2	N1	C5	110.8(5)	C15	C16	N12	106.4(5)
C2	N1	C6	117.5(5)	N3	C17	C18	111.7(5)
C5	N1	C6	131.7(5)	C19	C18	C17	111.6(5)
N1	C2	Ta1	119.3(4)	C20	C19	C18	114.4(6)
N3	C2	Ta1	136.3(4)	N14	C21	C22	111.7(5)
N3	C2	N1	104.2(5)	C21	C22	C23	112.3(5)
C2	N3	C4	110.8(5)	C24	C23	C22	114.3(6)
C2	N3	C17	123.6(5)	C26	N25	Ta1	165.8(4)
C4	N3	C17	125.4(5)	N25	C26	C27	108.6(6)
C5	C4	N3	107.3(5)	N25	C26	C28	109.8(6)
C4	C5	N1	106.8(5)	N25	C26	C29	107.6(5)
C7	C6	N1	125.0(5)	C27	C26	C28	111.9(8)
C7	C6	C11	123.7(5)	C27	C26	C29	109.0(7)
C11	C6	N1	111.3(5)	C28	C26	C29	109.8(7)
C6	C7	C8	117.7(5)	C31	N30	Ta1	119.4(4)
C7	C8	C9	121.2(5)	C32	N30	Ta1	134.5(4)
C10	C9	C8	117.5(5)	C32	N30	C31	106.1(4)
C9	C10	C11	124.2(5)				

Table A3-6. Torsion Angles for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ta1	C2	N3	C4	-176.3(5)	C7	C8	C9	C10	-0.9(9)
Ta1	C2	N3	C17	7.6(9)	C8	C9	C10	C11	0.7(9)
Ta1	C13	N14	C15	172.5(4)	C8	C9	C10	N12	179.9(5)
Ta1	C13	N14	C21	-4.6(8)	C9	C10	C11	Ta1	172.1(4)
Ta1	N25	C26	C27	74(2)	C9	C10	C11	C6	-0.4(8)
Ta1	N25	C26	C28	-163.5(17)	C9	C10	N12	C13	-177.4(5)
Ta1	N25	C26	C29	-44(2)	C9	C10	N12	C16	-0.1(9)
I1	Ta1	N25	C26	7(3)	C10	N12	C13	Ta1	4.0(6)
N1	C2	N3	C4	-1.3(6)	C10	N12	C13	N14	178.6(4)
N1	C2	N3	C17	-177.4(5)	C10	N12	C16	C15	-178.1(5)

N1	C6	C7	C8	-178.5(5)
N1	C6	C11	Ta1	6.0(6)
N1	C6	C11	C10	178.5(5)
C2	Ta1	N25	C26	66.9(19)
C2	N1	C5	C4	-1.1(7)
C2	N1	C6	C7	174.8(5)
C2	N1	C6	C11	-3.2(7)
C2	N3	C4	C5	0.7(7)
C2	N3	C17	C18	98.9(7)
N3	C4	C5	N1	0.2(7)
N3	C17	C18	C19	-175.9(6)
C4	N3	C17	C18	-76.6(8)
C5	N1	C2	Ta1	177.5(4)
C5	N1	C2	N3	1.5(6)
C5	N1	C6	C7	-3.0(10)
C5	N1	C6	C11	179.0(6)
C6	N1	C2	Ta1	-0.7(6)
C6	N1	C2	N3	-176.8(5)
C6	N1	C5	C4	176.8(6)
C6	C7	C8	C9	1.0(9)
C7	C6	C11	Ta1	-172.0(4)
C7	C6	C11	C10	0.5(8)
C11	Ta1	N25	C26	-2.8(19)
C11	C6	C7	C8	-0.8(9)
C11	C10	N12	C13	1.9(7)
C11	C10	N12	C16	179.2(5)
N12	C10	C11	Ta1	-7.2(6)
N12	C10	C11	C6	-179.7(5)
N12	C13	N14	C15	-0.7(6)
N12	C13	N14	C21	-177.8(5)
C13	Ta1	N25	C26	-72.5(19)
C13	N12	C16	C15	-0.7(6)
C13	N14	C15	C16	0.3(6)
C13	N14	C21	C22	96.2(6)
N14	C15	C16	N12	0.3(6)
N14	C21	C22	C23	-171.5(5)
C15	N14	C21	C22	-80.5(7)
C16	N12	C13	Ta1	-173.8(3)
C16	N12	C13	N14	0.8(6)
C17	N3	C4	C5	176.7(6)
C17	C18	C19	C20	-172.4(7)
C21	N14	C15	C16	177.3(5)
C21	C22	C23	C24	-58.3(8)
N30	Ta1	N25	C26	177.5(19)

Table A3-7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**).

Atom	*X*	*Y*	*z*	U(eq)
H4	5786	1766	3149	29
H5	5832	143	3781	24
H7	5135	-1465	4222	22
H8	4301	-2812	4652	26
H9	2649	-2763	4650	23
H15	-598	-1562	4305	18
H16	887	-2475	4601	19
H17A	3307	2560	2647	28
H17B	4321	2805	2328	28
H18A	3826	3131	4154	31
H18B	4803	3432	3786	31

H19A	3939	4475	2706	37
H19B	3016	4237	3199	37
H20A	3563	5670	3758	69
H20B	4598	5253	3987	69
H20C	3765	4916	4570	69
H21A	-90	950	3738	19
H21B	-928	329	4084	19
H22A	-1227	-376	2648	29
H22B	-309	98	2295	29
H23A	-990	1621	2336	33
H23B	-1657	936	1698	33
H24A	-2637	1747	2552	42
H24B	-1976	1579	3477	42
H24C	-2563	711	3007	42
H27A	1615	-1441	2127	80
H27B	1588	-1561	1041	80
H27C	827	-906	1474	80
H28A	1177	478	612	86
H28B	2016	27	105	86
H28C	2193	964	717	86
H29A	3560	-65	1419	57
H29B	3184	-1034	944	57
H29C	3334	-961	2035	57
H31A	1444	2897	2234	32
H31B	450	2475	2453	32
H31C	1180	1817	1977	32
H32A	654	2832	3987	42
H32B	1583	3377	3750	42
H32C	1632	2624	4571	42

Experimental

Single crystals of $C_{26}H_{40}N_6ITa$ (1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**13**) were crystallized via a saturated solution of complex 2 in benzene . A suitable crystal was selected and mounted on a 150um cryoloop and mounted on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.15 K during data collection. Using Olex2,[4] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using CGLS minimisation.[5,6]

Crystal Data for $C_{26}H_{40}N_6ITa$ (M =744.49): monoclinic, space group $P2_1/c$ (no. 14), a = 14.3134(5) Å, b = 14.0461(5) Å, c = 14.6772(5) Å, β = 95.1620(10)°, V = 2938.85(18) Å^3, Z = 4, T = 100.15 K, μ(CuKα) = 15.326 mm^{-1}, *Dcalc* = 1.683 g/mm^3, 27074 reflections measured ($6.2 \leq 2\Theta \leq 139.862$), 5465 unique ($R_{int}$ = 0.0508) which were used in all calculations. The final R_1 was 0.0491 ($I > 2\sigma(I)$) and wR_2 was 0.1370 (all data).

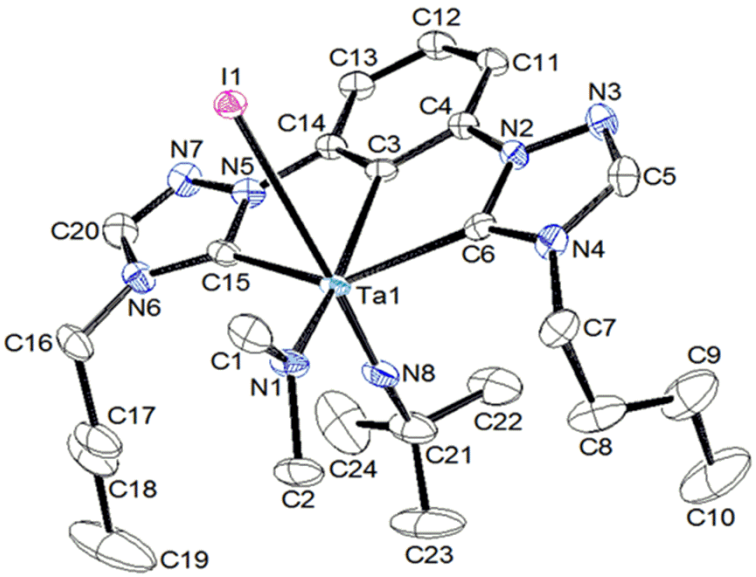


Figure A4. (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodo tantalum(V) (**15**).

Table A4-1. Crystal data and structure refinement for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**15**).

Empirical formula	$C_{48}H_{80}N_{16}I_2Ta_2$
Formula weight	1492.95
Temperature/K	100.13
Crystal system	triclinic
Space group	P-1
a/Å	10.6851(12)
b/Å	10.9572(12)
c/Å	24.299(3)
α/°	89.884(1)
β/°	84.039(1)
γ/°	86.730(1)
Volume/Å^3	2824.9(5)
Z	2
ρ_{calc}mg/mm^3	1.7550
m/mm^{-1}	5.010
F(000)	1452.5
Crystal size/mm^3	0.2 × 0.2 × 0.2
2Θ range for data collection	3.38 to 58.12°
Index ranges	$-14 \leq h \leq 14$, $-14 \leq k \leq 14$, $-33 \leq l \leq 33$
Reflections collected	34679
Independent reflections	13751[R(int) = 0.0301]
Data/restraints/parameters	13751/0/626
Goodness-of-fit on F^2	1.145
Final R indexes [I>=2σ (I)]	R_1 = 0.0241, wR_2 = N/A
Final R indexes [all data]	R_1 = 0.0252, wR_2 = 0.0617
Largest diff. peak/hole / e Å^{-3}	1.15/-1.08

Table A4-2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (15). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*X*	*Y*	*z*	U(eq)
Ta1	8218.15(11)	7121.62(11)	3909.71(5)	14.99(3)
Ta2	1511.99(11)	1982.59(10)	1130.96(5)	11.72(3)
I1	10993.73(18)	7665.30(18)	3706.82(8)	17.65(5)
I2	-1318.73(18)	2745.07(18)	1306.31(8)	17.97(5)
N1	8759(3)	5463(2)	4215.4(12)	20.6(6)
N2	8264(2)	7626(2)	2627.0(11)	16.3(5)
N3	8288(3)	7293(3)	2082.3(12)	21.9(6)
N4	8232(3)	5706(2)	2653.0(12)	20.1(5)
N5	8238(3)	9898(2)	4228.9(12)	19.4(5)
N6	8479(3)	9068(3)	5000.7(11)	21.2(6)
N7	8302(3)	10860(3)	4584.2(13)	23.8(6)
N8	6555(3)	7151(3)	4076.6(12)	24.8(6)
N9	3190(2)	1862(2)	1068.9(10)	15.1(5)
N10	1264(2)	2445(2)	2416.3(10)	14.8(5)
N11	1295(2)	517(2)	2372.6(11)	15.9(5)
N12	1200(3)	2079(3)	2958.5(11)	19.7(5)
N13	1447(2)	4779(2)	826.2(11)	15.4(5)
N14	1535(2)	3992(2)	31.3(11)	16.2(5)
N15	1481(3)	5765(2)	474.6(12)	19.7(5)
N16	1079(3)	379(2)	792.7(11)	17.4(5)
C1	9971(3)	4757(3)	4163.5(15)	25.4(7)
C2	7833(4)	4679(4)	4512.2(17)	32.2(8)
C3	8209(3)	8863(3)	3402.3(13)	16.3(6)
C4	8204(3)	8849(3)	2834.3(13)	16.7(6)
C5	8266(3)	6104(3)	2118.8(14)	23.2(7)
C6	8236(3)	6691(3)	2989.8(13)	16.8(6)
C7	8010(3)	4450(3)	2838.3(16)	24.7(7)
C8	6619(4)	4311(4)	2976(2)	40.5(10)
C9	5835(5)	4646(5)	2519(3)	56.3(14)
C10	4395(5)	4605(6)	2700(4)	82(2)
C11	8146(3)	9900(3)	2509.7(14)	20.1(6)
C12	8090(3)	11021(3)	2785.0(15)	24.1(7)
C13	8105(3)	11100(3)	3359.6(15)	22.0(7)
C14	8166(3)	10003(3)	3645.9(13)	17.5(6)
C15	8348(3)	8779(3)	4466.7(13)	19.3(6)
C16	8685(3)	8170(4)	5442.0(15)	27.7(8)
C17	7483(4)	7690(5)	5709.8(19)	44.2(12)

C18	6570(4)	8686(6)	5978(2)	58.7(16)
C19	5362(6)	8185(9)	6265(4)	121(4)
C20	8448(3)	10310(3)	5050.2(15)	26.3(7)
C21	5217(4)	7437(5)	4198.5(19)	41.2(11)
C22	4731(4)	7924(6)	3676(2)	66.4(19)
C23	4560(5)	6321(7)	4410(3)	85(3)
C24	5050(5)	8471(7)	4640(2)	77(2)
C25	4535(3)	2010(3)	1088.1(14)	21.2(6)
C26	4834(4)	3296(3)	882.8(18)	32.2(8)
C27	5302(3)	1032(4)	727.2(18)	31.8(8)
C28	4812(4)	1862(4)	1694.3(16)	37.2(10)
C29	1371(3)	3704(3)	1650.6(12)	13.4(5)
C30	1295(3)	3675(3)	2225.2(13)	14.9(6)
C31	1320(3)	1524(3)	2044.5(12)	13.7(5)
C32	1432(3)	-753(3)	2172.0(13)	16.8(6)
C33	2801(3)	-1126(3)	1976.1(14)	21.0(6)
C34	3683(3)	-1117(4)	2429.2(16)	29.1(8)
C35	5024(4)	-1586(4)	2218.5(19)	39.7(10)
C36	1217(3)	888(3)	2913.7(13)	20.5(6)
C37	1259(3)	4711(3)	2555.3(13)	18.6(6)
C38	1300(3)	5843(3)	2289.1(15)	22.3(7)
C39	1354(3)	5931(3)	1713.3(14)	19.6(6)
C40	1393(3)	4855(3)	1416.4(13)	15.5(6)
C41	1477(3)	3679(3)	571.6(13)	15.2(6)
C42	1539(3)	5244(3)	-9.5(14)	20.2(6)
C43	1654(3)	3123(3)	-435.9(13)	21.8(7)
C44	3007(4)	2600(3)	-559.3(15)	25.9(7)
C45	3944(4)	3548(4)	-746.8(17)	30.7(8)
C46	5304(4)	3026(4)	-812.2(19)	40.6(10)
C47	-109(3)	-233(3)	806.2(15)	25.1(7)
C48	2074(3)	-479(3)	524.2(15)	25.4(7)

Table A4-3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**15**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta1	13.66(6)	13.60(6)	17.10(6)	0.05(4)	0.69(4)	5.31(4)
Ta2	13.08(6)	9.23(6)	12.95(6)	-2.09(4)	-0.98(4)	0.27(4)
I1	13.72(9)	20.52(10)	18.36(9)	-1.28(7)	0.15(7)	1.56(7)
I2	13.85(9)	19.69(10)	20.65(10)	-1.49(7)	-2.90(7)	5.45(7)
N1	21.5(14)	15.8(13)	24.1(14)	0.4(10)	-1.1(11)	8.8(11)
N2	16.4(12)	15.8(12)	16.4(12)	2(1)	-2.5(9)	1.9(10)
N3	23.6(14)	22.7(14)	19.2(13)	3.9(11)	-4.3(11)	0.3(11)
N4	20.9(14)	15.1(13)	25.2(14)	-0.1(10)	-7.2(11)	1.3(11)
N5	18.0(13)	15.8(13)	23.2(14)	3(1)	1.6(10)	-0.9(10)
N6	18.4(13)	26.0(14)	17.5(13)	4.8(11)	2(1)	-0.6(11)
N7	22.0(14)	21.6(14)	26.6(15)	4.1(11)	0.1(11)	-5.6(11)
N8	21.3(14)	29.2(15)	23.3(14)	-0.5(12)	0.3(11)	11.5(12)
N9	14.7(12)	15.5(12)	15.0(12)	-0.3(9)	-1.3(9)	0.5(9)
N10	15.9(12)	14.0(12)	14.9(12)	-2.3(9)	-1.7(9)	1.6(9)
N11	18.1(13)	14.7(12)	14.8(12)	-2.6(10)	-0.2(9)	3.0(9)
N12	22.6(14)	21.0(13)	15.4(13)	-2.0(11)	-1.6(10)	2(1)
N13	16.9(12)	11.1(11)	18.2(13)	-2.0(9)	-1.2(10)	4.5(9)
N14	15.3(12)	15.1(12)	18.4(13)	-2.6(10)	-2.6(10)	4(1)
N15	20.7(13)	12.3(12)	26.1(14)	-1.4(10)	-2.1(11)	8.2(10)
N16	21.2(13)	13.1(12)	19.1(13)	-3.9(10)	-5.4(10)	-0.7(10)
C1	28.8(18)	18.7(16)	27.4(17)	6.5(13)	-1.8(14)	6.8(13)
C2	28.3(19)	25.9(18)	42(2)	-3.7(15)	-0.7(16)	19.9(16)
C3	13.2(14)	13.8(14)	21.4(15)	0.5(11)	0.3(11)	5.8(11)
C4	13.5(14)	15.6(14)	20.7(15)	2.4(11)	-1.6(11)	4.2(11)
C5	23.0(16)	23.0(16)	23.9(17)	4.1(13)	-6.7(13)	-3.5(13)
C6	11.7(13)	14.7(14)	24.2(16)	-0.1(11)	-3.8(11)	4.0(12)
C7	24.0(17)	14.3(15)	36.8(19)	-0.4(12)	-8.0(14)	0.9(13)
C8	25(2)	26.0(19)	69(3)	-2.3(15)	0.2(19)	11.5(19)
C9	37(3)	46(3)	90(4)	-9(2)	-24(3)	12(3)
C10	34(3)	72(4)	149(7)	-18(3)	-37(4)	26(4)
C11	19.2(15)	20.3(15)	20.6(15)	0.6(12)	-2.0(12)	7.8(12)
C12	26.1(17)	15.1(15)	30.2(18)	1.2(13)	0.4(13)	9.0(13)
C13	22.9(16)	13.4(14)	28.7(17)	1.5(12)	0.1(13)	3.7(12)
C14	15.7(14)	14.9(14)	21.0(15)	1.1(11)	0.7(11)	3.5(11)
C15	14.2(14)	23.1(16)	19.1(15)	2.1(12)	3.4(11)	4.2(12)
C16	26.1(18)	35(2)	20.3(16)	7.9(15)	-1.8(13)	8.5(14)
C17	27(2)	64(3)	39(2)	6(2)	-0.7(17)	31(2)
C18	29(2)	103(5)	39(3)	20(3)	7.5(19)	27(3)

C19	55(4)	181(9)	111(6)	39(5)	44(4)	100(6)
C20	23.7(17)	29.5(18)	24.8(17)	3.2(14)	0.4(13)	-5.0(14)
C21	21.8(19)	54(3)	46(2)	1.1(18)	2.8(17)	24(2)
C22	20(2)	110(5)	72(4)	-12(3)	-14(2)	51(4)
C23	20(2)	111(5)	123(6)	-15(3)	0(3)	79(5)
C24	39(3)	132(6)	52(3)	44(3)	3(2)	9(4)
C25	17.0(15)	19.2(15)	27.9(17)	-4.0(12)	-3.7(12)	1.9(13)
C26	24.2(18)	25.2(18)	48(2)	-8.1(14)	-2.9(16)	4.7(16)
C27	14.7(16)	31.7(19)	47(2)	4.5(14)	5.1(15)	-3.4(17)
C28	30(2)	57(3)	28(2)	-16.5(19)	-14.5(16)	7.1(18)
C29	12.9(13)	10.9(13)	16.4(14)	-0.5(10)	-1.2(10)	-0.2(10)
C30	13.3(13)	13.7(13)	17.3(14)	-1.5(10)	0.3(10)	-0.7(11)
C31	11.6(13)	12.6(13)	16.7(14)	-2(1)	0.4(10)	1.6(11)
C32	19.1(15)	11.1(13)	20.5(15)	-2.4(11)	-2.2(11)	1.5(11)
C33	21.0(16)	16.0(14)	25.4(16)	-1.4(12)	0.1(12)	0.3(12)
C34	20.9(17)	38(2)	28.0(18)	0.0(15)	-3.0(14)	4.6(15)
C35	22.8(19)	53(3)	43(2)	5.0(18)	-2.9(16)	4(2)
C36	23.9(16)	20.9(15)	16.6(15)	-2.2(12)	-0.9(12)	3.6(12)
C37	19.6(15)	17.5(15)	18.6(15)	-1.2(12)	-0.8(11)	-4.9(12)
C38	22.3(16)	15.2(15)	29.4(18)	-2.1(12)	-1.9(13)	-6.6(13)
C39	19.7(15)	11.0(13)	27.7(17)	-0.8(11)	-0.7(12)	-1.0(12)
C40	16.0(14)	13.4(13)	17.4(14)	-2.2(11)	-2.5(11)	-0.2(11)
C41	11.1(13)	15.2(14)	19.4(14)	-3.4(10)	-1.1(11)	1.7(11)
C42	19.6(15)	17.6(15)	23.4(16)	-0.6(12)	-2.2(12)	7.0(12)
C43	26.2(17)	26.2(17)	13.8(14)	-7.4(13)	-2.6(12)	-0.2(12)
C44	33.2(19)	23.2(17)	20.4(16)	-0.9(14)	0.6(14)	-3.1(13)
C45	25.9(18)	33(2)	30.9(19)	1.1(15)	4.5(14)	3.0(15)
C46	30(2)	47(3)	42(2)	1.6(18)	8.2(17)	-2.3(19)
C47	28.7(18)	18.1(15)	30.4(18)	-8.8(13)	-7.7(14)	-2.1(13)
C48	30.0(18)	16.6(15)	29.6(18)	2.9(13)	-5.7(14)	-8.1(13)

Table A4-5. Bond Lengths for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**15**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ta1	I1	3.0480(4)	N13	C40	1.432(4)
Ta1	N1	2.037(3)	N13	C41	1.353(4)
Ta1	N8	1.780(3)	N14	C41	1.352(4)
Ta1	C3	2.270(3)	N14	C42	1.375(4)
Ta1	C6	2.283(3)	N14	C43	1.474(4)
Ta1	C15	2.286(3)	N15	C42	1.303(4)
Ta2	I2	3.0779(4)	N16	C47	1.466(4)
Ta2	N9	1.781(3)	N16	C48	1.478(4)
Ta2	N16	2.039(3)	C3	C4	1.381(4)
Ta2	C29	2.262(3)	C3	C14	1.380(4)
Ta2	C31	2.266(3)	C4	C11	1.396(4)
Ta2	C41	2.302(3)	C7	C8	1.506(5)
N1	C1	1.465(4)	C8	C9	1.493(7)
N1	C2	1.478(4)	C9	C10	1.559(8)
N2	N3	1.371(4)	C11	C12	1.395(5)
N2	C4	1.428(4)	C12	C13	1.401(5)
N2	C6	1.350(4)	C13	C14	1.389(4)
N3	C5	1.308(4)	C16	C17	1.501(6)
N4	C5	1.366(4)	C17	C18	1.523(7)
N4	C6	1.356(4)	C18	C19	1.531(8)
N4	C7	1.471(4)	C21	C22	1.506(6)
N5	N7	1.374(4)	C21	C23	1.507(7)
N5	C14	1.431(4)	C21	C24	1.552(9)
N5	C15	1.358(4)	C25	C26	1.533(5)
N6	C15	1.360(4)	C25	C27	1.531(5)
N6	C16	1.478(4)	C25	C28	1.539(5)
N6	C20	1.365(5)	C29	C30	1.391(4)
N7	C20	1.301(5)	C29	C40	1.383(4)
N8	C21	1.446(5)	C30	C37	1.388(4)
N9	C25	1.462(4)	C32	C33	1.523(4)
N10	N12	1.372(4)	C33	C34	1.523(5)
N10	C30	1.425(4)	C34	C35	1.531(5)
N10	C31	1.350(4)	C37	C38	1.399(5)
N11	C31	1.359(4)	C38	C39	1.398(5)
N11	C32	1.470(4)	C39	C40	1.379(4)
N11	C36	1.370(4)	C43	C44	1.525(5)
N12	C36	1.309(4)	C44	C45	1.520(5)
N13	N15	1.376(3)	C45	C46	1.524(5)

Table A4-6. Bond Angles for (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**15**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ta1	I1	88.36(8)	C48	N16	C47	106.7(3)
N8	Ta1	I1	167.21(10)	C4	C3	Ta1	122.2(2)
N8	Ta1	N1	101.32(12)	C14	C3	Ta1	121.9(2)
C3	Ta1	I1	76.15(8)	C14	C3	C4	115.9(3)
C3	Ta1	N1	161.76(11)	C3	C4	N2	111.1(3)
C3	Ta1	N8	95.50(12)	C11	C4	N2	124.9(3)
C6	Ta1	I1	89.12(8)	C11	C4	C3	124.0(3)
C6	Ta1	N1	101.57(11)	N4	C5	N3	112.4(3)
C6	Ta1	N8	96.99(12)	N2	C6	Ta1	118.6(2)
C6	Ta1	C3	69.10(11)	N4	C6	Ta1	139.2(2)
C15	Ta1	I1	77.16(8)	N4	C6	N2	102.3(3)
C15	Ta1	N1	116.51(12)	C8	C7	N4	109.9(3)
C15	Ta1	N8	90.94(13)	C9	C8	C7	114.6(4)
C15	Ta1	C3	69.82(11)	C10	C9	C8	112.6(5)
C15	Ta1	C6	138.69(11)	C12	C11	C4	116.9(3)
N9	Ta2	I2	168.06(8)	C13	C12	C11	122.0(3)
N16	Ta2	I2	89.10(8)	C14	C13	C12	116.7(3)
N16	Ta2	N9	102.66(11)	C3	C14	N5	110.7(3)
C29	Ta2	I2	74.70(7)	C13	C14	N5	124.8(3)
C29	Ta2	N9	93.96(11)	C13	C14	C3	124.4(3)
C29	Ta2	N16	161.57(11)	N5	C15	Ta1	116.8(2)
C31	Ta2	I2	85.73(7)	N6	C15	Ta1	140.9(2)
C31	Ta2	N9	93.83(11)	N6	C15	N5	102.2(3)
C31	Ta2	N16	101.35(10)	C17	C16	N6	113.0(3)
C31	Ta2	C29	69.27(10)	C18	C17	C16	113.2(4)
C41	Ta2	I2	80.32(7)	C19	C18	C17	112.9(6)
C41	Ta2	N9	92.38(11)	N7	C20	N6	112.3(3)
C41	Ta2	N16	116.69(11)	C22	C21	N8	107.4(4)
C41	Ta2	C29	69.85(11)	C23	C21	N8	110.5(4)
C41	Ta2	C31	138.96(11)	C23	C21	C22	112.2(5)
C1	N1	Ta1	131.9(2)	C24	C21	N8	107.3(4)
C2	N1	Ta1	121.3(2)	C24	C21	C22	108.4(5)
C2	N1	C1	106.6(3)	C24	C21	C23	110.8(5)
C4	N2	N3	125.9(3)	C26	C25	N9	108.4(3)
C6	N2	N3	115.1(3)	C27	C25	N9	109.7(3)
C6	N2	C4	118.9(3)	C27	C25	C26	110.9(3)
C5	N3	N2	101.7(3)	C28	C25	N9	107.6(3)

C6	N4	C5	108.5(3)	C28	C25	C26	110.1(3)
C7	N4	C5	125.4(3)	C28	C25	C27	110.0(3)
C7	N4	C6	125.3(3)	C30	C29	Ta2	122.3(2)
C14	N5	N7	125.1(3)	C40	C29	Ta2	122.1(2)
C15	N5	N7	114.4(3)	C40	C29	C30	115.6(3)
C15	N5	C14	120.3(3)	C29	C30	N10	110.3(3)
C16	N6	C15	124.9(3)	C37	C30	N10	125.9(3)
C20	N6	C15	108.7(3)	C37	C30	C29	123.7(3)
C20	N6	C16	126.4(3)	N10	C31	Ta2	118.7(2)
C20	N7	N5	102.4(3)	N11	C31	Ta2	138.7(2)
C21	N8	Ta1	168.5(3)	N11	C31	N10	102.5(3)
C25	N9	Ta2	167.5(2)	C33	C32	N11	111.4(3)
C30	N10	N12	125.9(3)	C34	C33	C32	114.1(3)
C31	N10	N12	114.7(2)	C35	C34	C33	111.9(3)
C31	N10	C30	119.3(3)	N12	C36	N11	111.9(3)
C32	N11	C31	125.1(3)	C38	C37	C30	117.5(3)
C36	N11	C31	108.6(3)	C39	C38	C37	121.3(3)
C36	N11	C32	126.1(3)	C40	C39	C38	117.4(3)
C36	N12	N10	102.3(3)	C29	C40	N13	110.9(3)
C40	N13	N15	124.9(3)	C39	C40	N13	124.7(3)
C41	N13	N15	114.7(3)	C39	C40	C29	124.4(3)
C41	N13	C40	120.4(2)	N13	C41	Ta2	116.6(2)
C42	N14	C41	108.8(3)	N14	C41	Ta2	140.9(2)
C43	N14	C41	125.2(3)	N14	C41	N13	102.4(3)
C43	N14	C42	125.9(3)	N15	C42	N14	111.8(3)
C42	N15	N13	102.3(3)	C44	C43	N14	111.3(3)
C47	N16	Ta2	131.8(2)	C45	C44	C43	114.0(3)
C48	N16	Ta2	121.1(2)	C46	C45	C44	112.9(3)

Table A4-7. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for(1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodotantalum(V) (**15**).

Atom	*X*	*y*	*z*	U(eq)
H1a	10217(13)	4570(20)	4532.9(15)	38.1(11)
H1b	9894(8)	3996(12)	3962(10)	38.1(11)
H1c	10614(7)	5238(10)	3961(10)	38.1(11)
H2a	7780(20)	3930(13)	4298(6)	48.3(13)
H2b	8100(15)	4470(20)	4876(5)	48.3(13)
H2c	7004(7)	5119(11)	4560(11)	48.3(13)
H5	8273(3)	5576(3)	1808.7(14)	27.8(8)
H7a	8346(3)	3865(3)	2542.4(16)	29.7(8)
H7b	8456(3)	4267(3)	3168.9(16)	29.7(8)
H8a	6487(4)	3451(4)	3081(2)	48.6(12)
H8b	6320(4)	4829(4)	3302(2)	48.6(12)
H9a	6020(5)	5480(5)	2389(3)	67.5(17)
H9b	6069(5)	4075(5)	2205(3)	67.5(17)
H10a	4188(10)	3760(9)	2780(20)	123(3)
H10b	4169(11)	5120(40)	3029(14)	123(3)
H10c	3921(5)	4910(50)	2399(9)	123(3)
H11	8144(3)	9854(3)	2119.4(14)	24.1(8)
H12	8040(3)	11753(3)	2576.4(15)	28.9(8)
H13	8074(3)	11866(3)	3544.4(15)	26.3(8)
H16a	9239(3)	7477(4)	5282.8(15)	33.2(9)
H16b	9125(3)	8561(4)	5728.4(15)	33.2(9)
H17a	7066(4)	7262(5)	5426.9(19)	53.1(14)
H17b	7688(4)	7084(5)	5994.7(19)	53.1(14)
H18a	6995(4)	9130(6)	6254(2)	70.4(19)
H18b	6344(4)	9278(6)	5692(2)	70.4(19)
H19a	4890(40)	7820(70)	5988(6)	182(6)
H19b	5581(7)	7560(60)	6530(20)	182(6)
H19c	4840(40)	8852(17)	6460(30)	182(6)
H20	8524(3)	10726(3)	5386.7(15)	31.6(9)
H22a	5190(30)	8640(30)	3550(11)	100(3)
H22b	4850(40)	7290(15)	3389(6)	100(3)
H22c	3831(11)	8160(40)	3749(5)	100(3)
H23a	4770(40)	5645(17)	4147(12)	128(4)
H23b	4830(40)	6090(30)	4770(11)	128(4)
H23c	3646(5)	6504(18)	4450(20)	128(4)
H24a	5400(40)	8182(17)	4977(8)	115(3)
H24b	5490(40)	9183(19)	4496(9)	115(3)
H24c	4151(6)	8700(30)	4726(16)	115(3)

H26a	4600(30)	3402(10)	506(5)	48.3(12)
H26b	4360(20)	3906(3)	1128(7)	48.3(12)
H26c	5739(6)	3401(10)	883(12)	48.3(12)
H27a	5120(20)	220(4)	875(7)	47.7(12)
H27b	5070(20)	1092(18)	348(3)	47.7(12)
H27c	6203(3)	1157(17)	728(10)	47.7(12)
H28a	4310(20)	2488(19)	1923(3)	55.9(14)
H28b	4590(30)	1049(12)	1826(4)	55.9(14)
H28c	5711(7)	1960(30)	1720(3)	55.9(14)
H32a	1124(3)	-1304(3)	2473.4(13)	20.2(7)
H32b	910(3)	-842(3)	1862.6(13)	20.2(7)
H33a	2841(3)	-1958(3)	1815.2(14)	25.2(8)
H33b	3104(3)	-563(3)	1678.5(14)	25.2(8)
H34a	3702(3)	-273(4)	2571.6(16)	34.9(9)
H34b	3356(3)	-1637(4)	2739.3(16)	34.9(9)
H35a	5013(6)	-2429(11)	2087(13)	59.5(15)
H35b	5354(12)	-1068(19)	1914(9)	59.5(15)
H35c	5564(8)	-1560(30)	2520(4)	59.5(15)
H36	1180(3)	346(3)	3219.7(13)	24.6(8)
H37	1209(3)	4654(3)	2947.0(13)	22.4(7)
H38	1290(3)	6568(3)	2504.0(15)	26.8(8)
H39	1364(3)	6701(3)	1533.4(14)	23.5(7)
H42	1579(3)	5676(3)	-349.6(14)	24.3(8)
H43a	1091(3)	2448(3)	-346.7(13)	26.2(8)
H43b	1386(3)	3545(3)	-768.5(13)	26.2(8)
H44a	3272(4)	2196(3)	-222.1(15)	31.1(9)
H44b	3032(4)	1967(3)	-851.1(15)	31.1(9)
H45a	3734(4)	3892(4)	-1105.2(17)	36.9(9)
H45b	3862(4)	4224(4)	-473.5(17)	36.9(9)
H46a	5564(11)	2810(30)	-448(2)	60.8(15)
H46b	5371(7)	2294(18)	-1047(12)	60.8(15)
H46c	5852(6)	3638(12)	-984(13)	60.8(15)
H47a	-276(13)	-420(20)	427.6(16)	37.7(11)
H47b	-46(10)	-993(13)	1018(10)	37.7(11)
H47c	-798(5)	306(10)	982(10)	37.7(11)
H48a	2104(18)	-1239(10)	737(7)	38.1(11)
H48b	1887(14)	-660(20)	147(4)	38.1(11)
H48c	2890(5)	-109(11)	511(10)	38.1(11)

Experimental

Single crystals of $C_{48}H_{80}N_{16}I_2Ta_2$ (1,3-bis(3-butyltriazol-1-yl-2-idene)-2-phenylene) (*t*-butylimido)(dimethylamido)iodo tantalum(V) were crystallized via layering Et_2O to a saturated solution in toluene. A suitable crystal was selected and mounted on a 150um mitogen mount on a Bruker Smart APEX II diffractometer. The crystal was kept at 100.13 K during data collection. Using Olex2,[4] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the olex2.refine refinement package using Gauss-Newton minimisation.[5,7]

Crystal Data for $C_{48}H_{80}N_{16}I_2Ta_2$ (M =1492.95): triclinic, space group P-1 (no. 2), a = 10.6851(12) Å, b = 10.9572(12) Å, c = 24.299(3) Å, α = 89.884(1)°, β = 84.039(1)°, γ = 86.730(1)°, V = 2824.9(5) Å^3, Z = 2, T = 100.13 K, μ(N/A) = 5.010 mm^{-1}, *Dcalc* = 1.7550 g/mm^3, 34679 reflections measured ($3.38 \leq 2\Theta \leq 58.12$), 13751 unique ($R_{int}$ = 0.0301) which were used in all calculations. The final R_1 was 0.0241 (I>=2u(I)) and wR_2 was 0.0617 (all data).

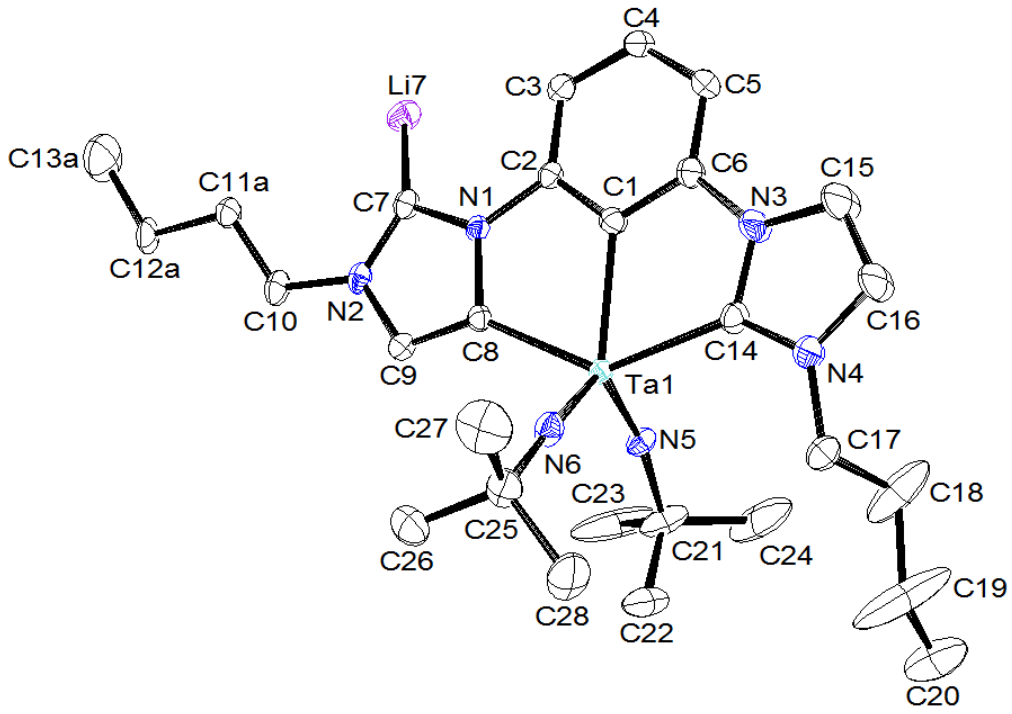


Figure A5. 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**)

Table A5-1. Crystal data and structure refinement for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**).

Empirical formula	$C_{28}H_{43}N_6OTaF_{0.25}Cl_{0.25}Si_{0.25}Br_{0.25}Li_{0.25}$
Formula weight	702.98
Temperature/K	100.08
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.095(3)
b/Å	15.178(3)
c/Å	17.651(4)
α/°	90
β/°	93.664(2)
γ/°	90
Volume/Å^3	2966.4(11)
Z	4
ρ_{calc}mg/mm^3	1.574
m/mm^{-1}	4.107
F(000)	1414.0
Crystal size/mm^3	0.5 × 0.5 × 0.5
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	3.542 to 57.988°
Index ranges	$-14 \leq h \leq 15$, $-20 \leq k \leq 20$, $-22 \leq l \leq 23$
Reflections collected	34837
Independent reflections	7427[R(int) = 0.0503]
Data/restraints/parameters	7427/0/382
Goodness-of-fit on F^2	1.229
Final R indexes [I>=2σ (I)]	R_1 = 0.0316, wR_2 = 0.0748
Final R indexes [all data]	R_1 = 0.0373, wR_2 = 0.0799
Largest diff. peak/hole / e Å^{-3}	1.35/-1.16

Table A5-2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement

Parameters ($Å^2 \times 10^3$) for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene bis(*t*-butylimido)tantalum(V) (**17**). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Ta1	9365.2(2)	8440.2(2)	8080.6(2)	14.13(5)
N1	9022(3)	10107.5(19)	9171.5(17)	16.0(6)
N2	10356(3)	11100(2)	9103.2(18)	19.1(6)
N3	6894(3)	7532(2)	8474(2)	28.2(8)
N4	7561(3)	6676(2)	7629(2)	24.6(7)
N5	10672(3)	7809(2)	8525.7(18)	19.5(6)
N6	9388(3)	8707(2)	7073.0(19)	22.3(7)
C1	7901(3)	8831(2)	8866(2)	18.8(7)
C2	7983(3)	9588(2)	9310(2)	16.3(7)
C3	7139(3)	9795(2)	9840(2)	20.0(7)
C4	6188(4)	9209(3)	9929(2)	22.6(8)
C5	6054(4)	8443(3)	9491(2)	22.2(8)
C6	6913(4)	8283(3)	8965(2)	21.7(8)
C7	9342(3)	10908(2)	9473(2)	18.7(7)
C8	9810(3)	9766(2)	8633(2)	16.6(7)
C9	10652(3)	10421(2)	8615(2)	18.0(7)
C10	11090(4)	11910(3)	9211(2)	24.7(8)
C11	10280(8)	12725(5)	9111(6)	27.8(18)
C12	11038(11)	13580(6)	9210(7)	36(2)
C13	11669(11)	13676(7)	10003(8)	41(3)
C11A	10557(8)	12680(5)	9556(6)	25.2(17)
C12A	11449(10)	13464(6)	9615(8)	28.0(19)
C13A	10904(13)	14243(8)	10032(8)	55(3)
C14	7849(4)	7418(2)	8029(2)	20.2(7)
C15	6039(5)	6870(4)	8352(3)	43.1(13)
C16	6465(4)	6331(3)	7818(3)	39.2(12)
C17	8366(4)	6243(3)	7122(2)	26.6(8)
C18	8891(8)	5404(4)	7472(3)	67(2)
C19	9896(8)	5032(7)	7017(5)	115(5)
C20	10859(13)	4451(9)	7224(7)	57(3)
C20A	9974(14)	3980(9)	7576(8)	56(3)
C21	11784(4)	7302(3)	8539(3)	36.1(11)
C22	12226(4)	7221(4)	7741(3)	38.1(11)
C23	12735(5)	7740(7)	9068(5)	99(4)

C24	11553(8)	6359(5)	8839(4)	78(3)
C25	9570(4)	8900(3)	6289(2)	28.2(9)
C26	10559(5)	9607(3)	6250(3)	38.1(11)
C27	8386(5)	9234(4)	5901(3)	47.2(13)
C28	10002(6)	8073(4)	5883(3)	48.8(15)
Li7	9063(7)	11345(5)	10587(4)	27.7(15)

Table A5-3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
Ta1	15.50(8)	13.27(8)	13.71(8)	-1.72(5)	1.48(5)	-0.54(5)
N1	20.0(15)	13.4(14)	15.0(14)	0.7(11)	3.5(11)	0.7(11)
N2	21.8(16)	12.8(14)	22.1(15)	-1.4(12)	-2.5(12)	-2.7(12)
N3	23.4(17)	27.7(18)	34.4(19)	-11.7(15)	8.0(14)	-10.5(14)
N4	25.1(17)	22.2(17)	26.8(18)	-7.1(13)	4.5(14)	-4.7(13)
N5	21.2(16)	17.8(15)	19.1(15)	-4.6(12)	-2.0(12)	2.2(12)
N6	30.3(18)	17.7(15)	18.8(15)	-1.1(12)	1.3(13)	-1.5(13)
C1	16.0(17)	19.7(17)	20.7(17)	-1.8(14)	1.9(13)	-1.4(14)
C2	16.8(16)	14.9(16)	17.1(16)	-0.3(13)	-1.1(13)	0.7(13)
C3	23.3(18)	18.0(17)	18.9(17)	-0.2(14)	2.0(14)	2.2(14)
C4	21.1(18)	22.5(19)	24.9(19)	1.3(15)	6.4(15)	3.1(15)
C5	18.0(18)	22.3(19)	27(2)	0.8(15)	4.2(15)	-2.5(14)
C6	20.8(18)	19.5(18)	25.0(19)	-4.6(15)	2.5(15)	-3.8(14)
C7	21.4(18)	15.9(16)	18.5(17)	-1.4(13)	-2.4(14)	-0.8(14)
C8	18.8(17)	14.8(16)	16.3(16)	1.6(13)	2.1(13)	-0.1(13)
C9	18.4(17)	17.7(17)	17.8(17)	-0.8(13)	-0.2(13)	0.3(13)
C10	27(2)	15.2(17)	31(2)	-2.0(15)	-3.9(16)	-5.5(15)
C11	31(5)	19(4)	31(5)	-6(4)	-11(4)	-2(3)
C12	51(6)	11(4)	45(6)	3(4)	-12(5)	-11(4)
C13	50(7)	25(5)	49(7)	-15(5)	17(6)	-16(5)
C11A	32(5)	16(4)	29(5)	-4(3)	9(4)	-4(3)
C12A	38(6)	13(4)	33(6)	-3(4)	4(5)	-10(4)
C13A	72(9)	34(6)	59(7)	-11(5)	11(6)	-13(6)
C14	21.7(18)	17.7(17)	21.0(17)	-3.9(14)	-0.3(14)	-2.0(14)
C15	35(3)	44(3)	53(3)	-28(2)	18(2)	-23(2)
C16	33(2)	37(3)	49(3)	-22(2)	15(2)	-21(2)
C17	32(2)	22.8(19)	25(2)	-9.1(16)	4.0(16)	-2.2(17)

C18	118(6)	43(3)	34(3)	-18(2)	-29(3)	41(4)
C19	84(5)	134(8)	118(7)	-105(6)	-66(5)	80(6)
C20	75(9)	62(8)	35(6)	-10(5)	-2(6)	33(7)
C20A	63(8)	45(7)	57(7)	-9(6)	-12(6)	29(6)
C21	29(2)	44(3)	34(2)	-17(2)	-9.3(18)	19(2)
C22	27(2)	48(3)	40(3)	-18(2)	4.9(19)	6(2)
C23	29(3)	167(9)	96(6)	-100(6)	-27(3)	41(4)
C24	129(7)	59(4)	49(4)	16(3)	22(4)	68(5)
C25	41(2)	27(2)	16.9(18)	0.9(15)	4.3(17)	0.0(18)
C26	47(3)	35(2)	35(2)	3(2)	17(2)	-5(2)
C27	51(3)	64(4)	25(2)	11(2)	-8(2)	5(3)
C28	87(5)	33(3)	28(2)	-8(2)	21(3)	-3(3)
Li7	29(4)	26(3)	29(4)	-7(3)	0(3)	2(3)

Table A5-4. Bond Lengths for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**).

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ta1	N5	1.869(3)	C7	Li7	2.117(8)
Ta1	N6	1.826(3)	C8	C9	1.366(5)
Ta1	C1	2.281(4)	C8	Li7[1]	2.467(8)
Ta1	C8	2.277(4)	C10	C11	1.534(10)
Ta1	C14	2.286(4)	C10	C11A	1.460(9)
Ta1	Li7[1]	2.855(7)	C11	C12	1.550(12)
N1	C2	1.431(5)	C12	C13	1.532(16)
N1	C7	1.364(5)	C11A	C12A	1.548(12)
N1	C8	1.428(4)	C12A	C13A	1.537(15)
N2	C7	1.367(5)	C15	C16	1.356(7)
N2	C9	1.395(5)	C17	C18	1.516(7)
N2	C10	1.480(5)	C18	C19	1.524(11)
N3	C6	1.433(5)	C19	C20	1.415(13)
N3	C14	1.369(5)	C19	C20A	1.876(18)
N3	C15	1.388(5)	C21	C22	1.526(7)
N4	C14	1.356(5)	C21	C23	1.518(7)
N4	C16	1.385(6)	C21	C24	1.553(9)
N4	C17	1.460(5)	C21	Li7[1]	2.769(8)
N5	C21	1.452(5)	C23	Li7[1]	2.536(9)
N5	Li7[1]	2.031(8)	C25	C26	1.540(7)
N6	C25	1.441(5)	C25	C27	1.529(7)

C1	C2	1.390(5)	C25	C28	1.536(6)
C1	C6	1.396(5)	Li7	Ta1[1]	2.855(7)
C2	C3	1.401(5)	Li7	N5[1]	2.031(8)
C3	C4	1.397(5)	Li7	C8[1]	2.467(8)
C4	C5	1.398(6)	Li7	C21[1]	2.769(8)
C5	C6	1.393(5)	Li7	C23[1]	2.536(9)

[1]2-X,2-Y,2-Z

Table A5-5. Bond Angles for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N5	Ta1	C1	116.21(14)	C9	C8	N1	101.6(3)
N5	Ta1	C8	97.57(13)	C9	C8	Li7[1]	100.8(3)
N5	Ta1	C14	102.60(14)	C8	C9	N2	109.5(3)
N5	Ta1	Li7[1]	45.21(17)	N2	C10	C11	110.0(4)
N6	Ta1	N5	117.68(15)	C11A	C10	N2	119.0(5)
N6	Ta1	C1	126.09(15)	C10	C11	C12	110.7(7)
N6	Ta1	C8	101.82(14)	C13	C12	C11	113.3(9)
N6	Ta1	C14	99.68(15)	C10	C11A	C12A	111.7(7)
N6	Ta1	Li7[1]	137.0(2)	C13A	C12A	C11A	110.8(8)
C1	Ta1	C14	69.50(14)	N3	C14	Ta1	119.1(3)
C1	Ta1	Li7[1]	83.74(18)	N4	C14	Ta1	137.1(3)
C8	Ta1	C1	69.69(13)	N4	C14	N3	103.8(3)
C8	Ta1	C14	139.10(13)	C16	C15	N3	106.2(4)
C8	Ta1	Li7[1]	56.10(17)	C15	C16	N4	106.8(4)
C14	Ta1	Li7[1]	121.27(19)	N4	C17	C18	111.3(4)
C7	N1	C2	128.1(3)	C17	C18	C19	111.8(7)
C7	N1	C8	115.3(3)	C18	C19	C20A	92.7(8)
C8	N1	C2	116.6(3)	C20	C19	C18	131.3(10)
C7	N2	C9	111.7(3)	N5	C21	C22	110.5(4)
C7	N2	C10	125.3(3)	N5	C21	C23	109.5(4)
C9	N2	C10	122.9(3)	N5	C21	C24	109.6(5)
C14	N3	C6	117.8(3)	N5	C21	Li7[1]	45.4(2)
C14	N3	C15	111.5(4)	C22	C21	C24	108.1(4)
C15	N3	C6	130.7(4)	C22	C21	Li7[1]	135.7(4)
C14	N4	C16	111.7(4)	C23	C21	C22	110.6(5)
C14	N4	C17	124.1(3)	C23	C21	C24	108.5(6)

C16	N4	C17	123.9(4)	C23	C21	Li7[1]	65.1(3)
Ta1	N5	Li7[1]	94.0(3)	C24	C21	Li7[1]	115.0(4)
C21	N5	Ta1	156.0(3)	C21	C23	Li7[1]	82.0(3)
C21	N5	Li7[1]	104.0(3)	N6	C25	C26	109.1(4)
C25	N6	Ta1	172.7(3)	N6	C25	C27	109.2(4)
C2	C1	Ta1	122.3(3)	N6	C25	C28	110.5(4)
C2	C1	C6	116.5(3)	C27	C25	C26	110.1(4)
C6	C1	Ta1	121.1(3)	C27	C25	C28	110.3(4)
C1	C2	N1	112.6(3)	C28	C25	C26	107.6(4)
C1	C2	C3	122.6(3)	N5[1]	Li7	Ta1[1]	40.76(16)
C3	C2	N1	124.8(3)	N5[1]	Li7	C7	153.1(4)
C4	C3	C2	118.3(3)	N5[1]	Li7	C8[1]	87.7(3)
C3	C4	C5	121.5(4)	N5[1]	Li7	C21[1]	30.59(17)
C6	C5	C4	117.4(4)	N5[1]	Li7	C23[1]	63.0(2)
C1	C6	N3	112.3(3)	C7	Li7	Ta1[1]	133.1(3)
C5	C6	N3	123.9(4)	C7	Li7	C8[1]	101.8(3)
C5	C6	C1	123.8(4)	C7	Li7	C21[1]	145.6(4)
N1	C7	N2	101.8(3)	C7	Li7	C23[1]	124.0(4)
N1	C7	Li7	126.3(3)	C8[1]	Li7	Ta1[1]	50.02(16)
N2	C7	Li7	123.3(3)	C8[1]	Li7	C21[1]	112.0(3)
Ta1	C8	Li7[1]	73.9(2)	C8[1]	Li7	C23[1]	128.2(4)
N1	C8	Ta1	118.7(2)	C21[1]	Li7	Ta1[1]	70.58(19)
N1	C8	Li7[1]	100.8(3)	C23[1]	Li7	Ta1[1]	100.9(3)
C9	C8	Ta1	139.7(3)	C23[1]	Li7	C21[1]	32.88(18)

[1]2-X,2-Y,2-Z

Table A5-6. Torsion Angles for1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**).

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ta1	N5	C21	C22	2.9(10)	C7	N2	C10	C11A	-18.9(7)
Ta1	N5	C21	C23	125.0(8)	C8	Ta1	N5	C21	-116.6(8)
Ta1	N5	C21	C24	-116.2(8)	C8	Ta1	N5	Li7[1]	22.4(3)
Ta1	N5	C21	Li7[1]	137.6(9)	C8	N1	C2	C1	-1.8(4)
Ta1	C1	C2	N1	4.4(4)	C8	N1	C2	C3	177.1(3)
Ta1	C1	C2	C3	-174.5(3)	C8	N1	C7	N2	1.4(4)
Ta1	C1	C6	N3	-5.6(5)	C8	N1	C7	Li7	-146.9(4)
Ta1	C1	C6	C5	173.5(3)	C9	N2	C7	N1	-1.9(4)

Ta1	C8	C9	N2	177.9(3)	C9	N2	C7	Li7	147.7(4)
N1	C2	C3	C4	-178.1(3)	C9	N2	C10	C11	129.2(6)
N1	C8	C9	N2	-0.8(4)	C9	N2	C10	C11A	163.1(6)
N2	C10	C11	C12	-179.1(7)	C10	N2	C7	N1	179.8(3)
N2	C10	C11A	C12A	-179.4(7)	C10	N2	C7	Li7	-30.6(6)
N3	C15	C16	N4	0.0(7)	C10	N2	C9	C8	-179.9(3)
N4	C17	C18	C19	-169.9(5)	C10	C11	C12	C13	-62.4(12)
N5	C21	C23	Li7[1]	9.8(5)	C10	C11A	C12A	C13A	-175.8(9)
N6	Ta1	N5	C21	-9.0(8)	C11	C10	C11A	C12A	-97.9(12)
N6	Ta1	N5	Li7[1]	130.0(3)	C11A	C10	C11	C12	67.9(10)
C1	Ta1	N5	C21	172.3(7)	C14	Ta1	N5	C21	99.2(8)
C1	Ta1	N5	Li7[1]	-48.7(3)	C14	Ta1	N5	Li7[1]	-121.8(3)
C1	C2	C3	C4	0.8(6)	C14	N3	C6	C1	4.5(6)
C2	N1	C7	N2	-176.4(3)	C14	N3	C6	C5	-174.6(4)
C2	N1	C7	Li7	35.3(6)	C14	N3	C15	C16	-0.2(7)
C2	N1	C8	Ta1	-1.4(4)	C14	N4	C16	C15	0.3(6)
C2	N1	C8	C9	177.7(3)	C14	N4	C17	C18	105.8(5)
C2	N1	C8	Li7[1]	-78.8(3)	C15	N3	C6	C1	-174.7(5)
C2	C1	C6	N3	178.8(3)	C15	N3	C6	C5	6.2(8)
C2	C1	C6	C5	-2.1(6)	C15	N3	C14	Ta1	177.8(4)
C2	C3	C4	C5	-1.5(6)	C15	N3	C14	N4	0.3(5)
C3	C4	C5	C6	0.5(6)	C16	N4	C14	Ta1	-177.2(4)
C4	C5	C6	N3	-179.6(4)	C16	N4	C14	N3	-0.4(5)
C4	C5	C6	C1	1.4(6)	C16	N4	C17	C18	-67.3(6)
C6	N3	C14	Ta1	-1.5(5)	C17	N4	C14	Ta1	9.0(7)
C6	N3	C14	N4	-179.0(4)	C17	N4	C14	N3	-174.2(4)
C6	N3	C15	C16	179.0(5)	C17	N4	C16	C15	174.1(5)
C6	C1	C2	N1	179.9(3)	C17	C18	C19	C20	158.2(12)
C6	C1	C2	C3	0.9(6)	C17	C18	C19	C20A	-170.7(6)
C7	N1	C2	C1	176.0(3)	C22	C21	C23	Li7[1]	131.9(4)
C7	N1	C2	C3	-5.1(6)	C24	C21	C23	Li7[1]	-109.7(4)
C7	N1	C8	Ta1	-179.5(2)	Li7[1]	Ta1	N5	C21	-139.0(9)
C7	N1	C8	C9	-0.4(4)	Li7[1]	N5	C21	C22	-134.7(4)
C7	N1	C8	Li7[1]	103.1(3)	Li7[1]	N5	C21	C23	-12.6(7)
C7	N2	C9	C8	1.8(4)	Li7[1]	N5	C21	C24	106.3(5)
C7	N2	C10	C11	-52.7(6)	Li7[1]	C8	C9	N2	-104.3(3)

[1]2-X,2-Y,2-Z

Table A5-7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1,3-bis(3-butylimidazol-1-yl-2-idene)-2-phenylene) bis(*t*-butylimido)tantalum(V) (**17**).

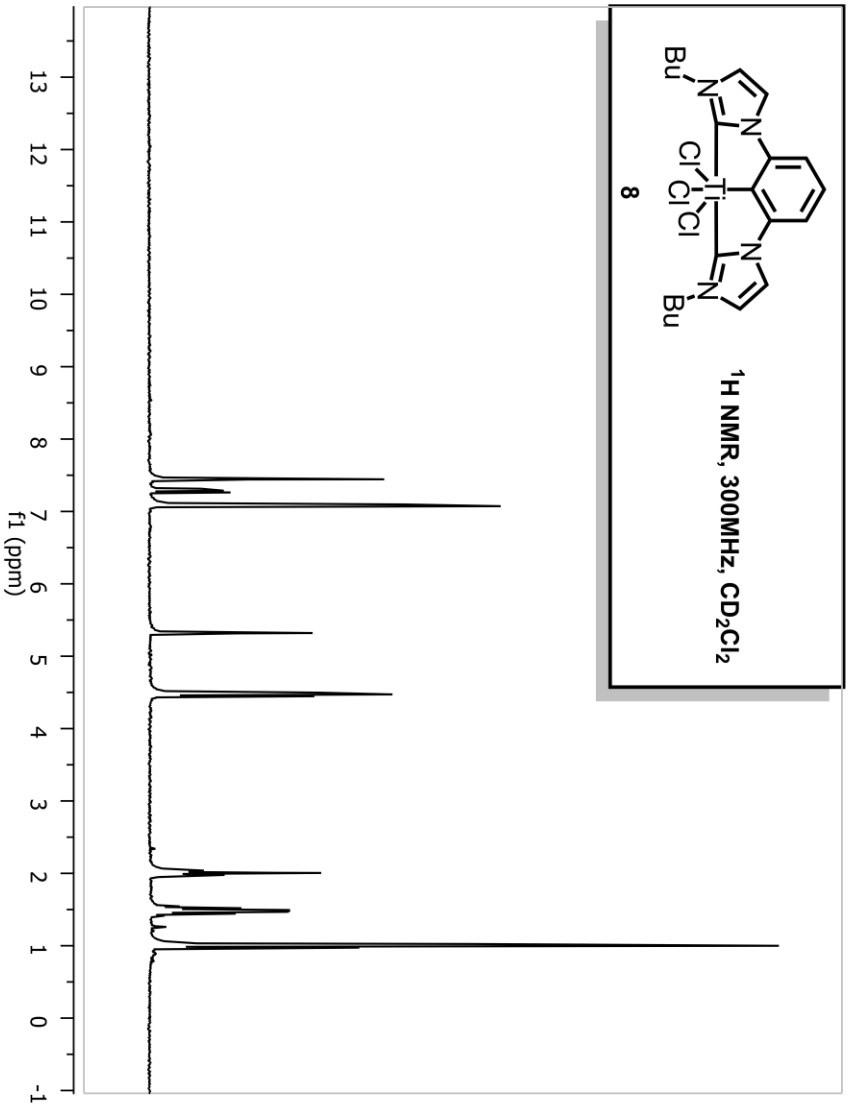
Atom	***x***	***y***	***z***	**U(eq)**
H3	7212	10320	10132	24
H4	5619	9333	10295	27
H5	5403	8047	9550	27
H9	11334	10415	8316	22
H10A	11717	11924	8837	30
H10B	11500	11910	9726	30
H10C	11980(90)	11770(70)	9460(60)	30
H10D	11360(90)	12190(70)	8650(60)	30
H11A	9661	12713	9491	33
H11B	9859	12717	8599	33
H12A	11655	13585	8829	44
H12B	10502	14094	9108	44
H13A	12359	13273	10054	61
H13B	11099	13534	10387	61
H13C	11953	14284	10075	61
H11C	10317	12524	10070	30
H11D	9820	12857	9247	30
H13D	10146	14424	9761	82
H13E	11473	14738	10050	82
H13F	10747	14065	10550	82
H15	5303	6808	8595	52
H16	6084	5815	7613	47
H17A	9031	6649	7013	32
H17B	7913	6101	6636	32
H18A	8242	4959	7497	80
H18B	9215	5526	7997	80
H19A	10651	5381	7072	138
H19B	9647	4943	6474	138
H20A	11354	4703	7651	86
H20B	11357	4368	6791	86
H20C	10533	3882	7375	86
H20D	10050(150)	3960(110)	8050(100)	84
H20E	9180(160)	3590(110)	7660(90)	84
H22A	11607	6926	7410	57

H22B	12972	6874	7759	57
H22C	12381	7809	7540	57
H23A	12929	8322	8868	148
H23B	13465	7376	9106	148
H23C	12424	7807	9572	148
H24A	11251	6397	9348	118
H24B	12309	6024	8862	118
H24C	10952	6062	8497	118
H26A	10303	10145	6500	57
H26B	10694	9734	5718	57
H26C	11311	9390	6507	57
H27A	7753	8790	5947	71
H27B	8497	9343	5362	71
H27C	8148	9782	6143	71
H28A	10749	7857	6145	73
H28B	10153	8221	5357	73
H28C	9379	7616	5887	73

NMR SPECTRA

7
^{1}H NMR, 300MHz, CD_2Cl_2
* = Toluene
*
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

^{13}C NMR, 300MHz, CD_2Cl_2
* = Toluene
7
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0


Bu
N
N
Cl
Ti
Cl
Cl
N
N
Bu
8
^{1}H NMR, 300MHz, CD_2Cl_2
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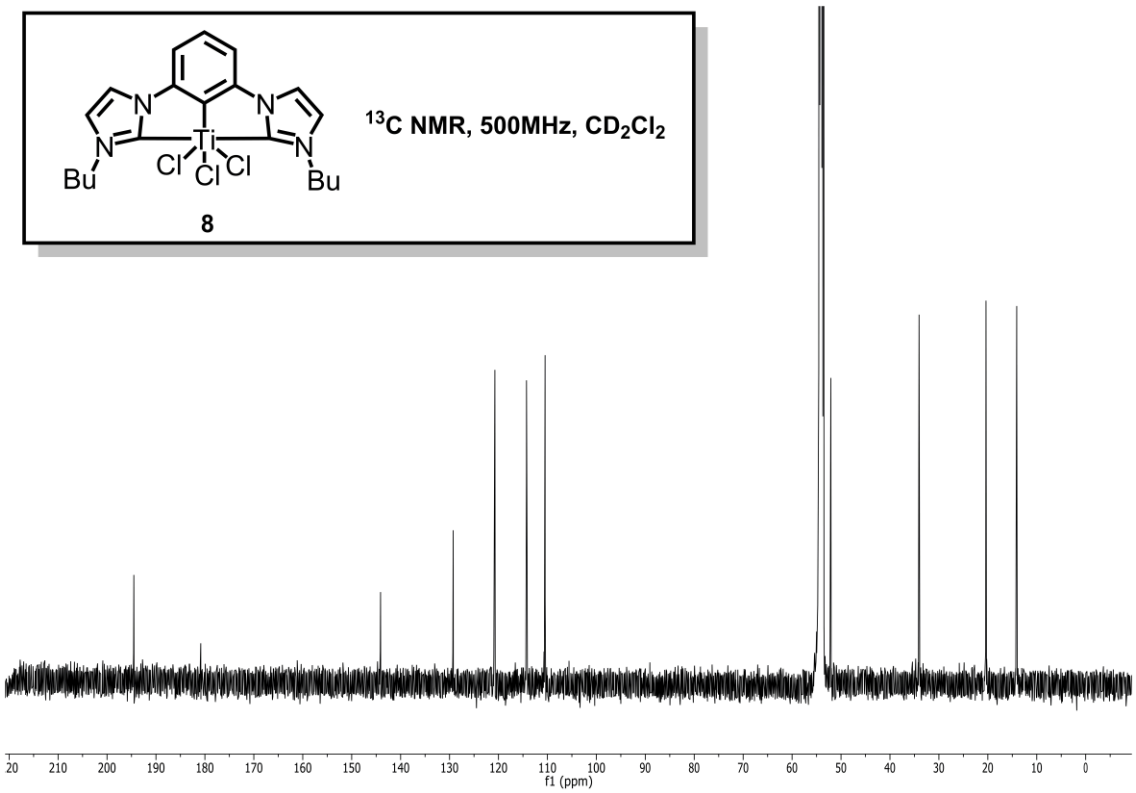
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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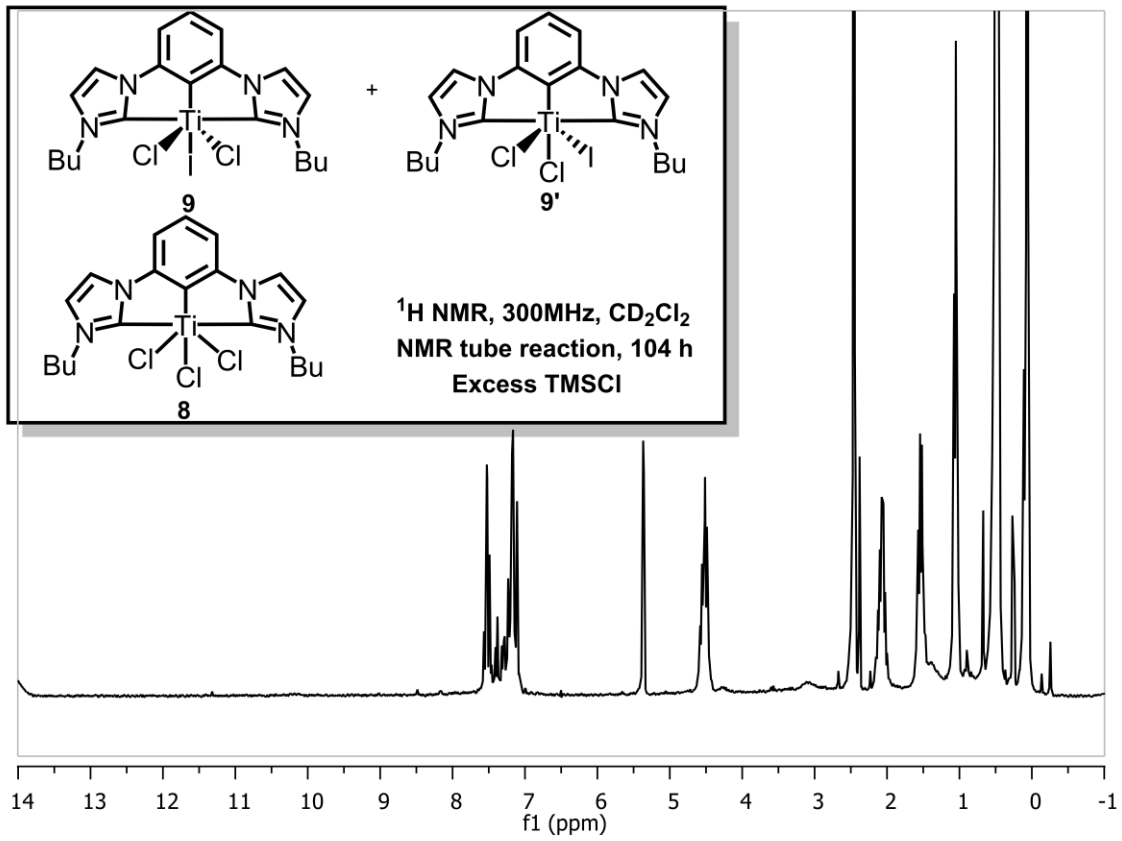
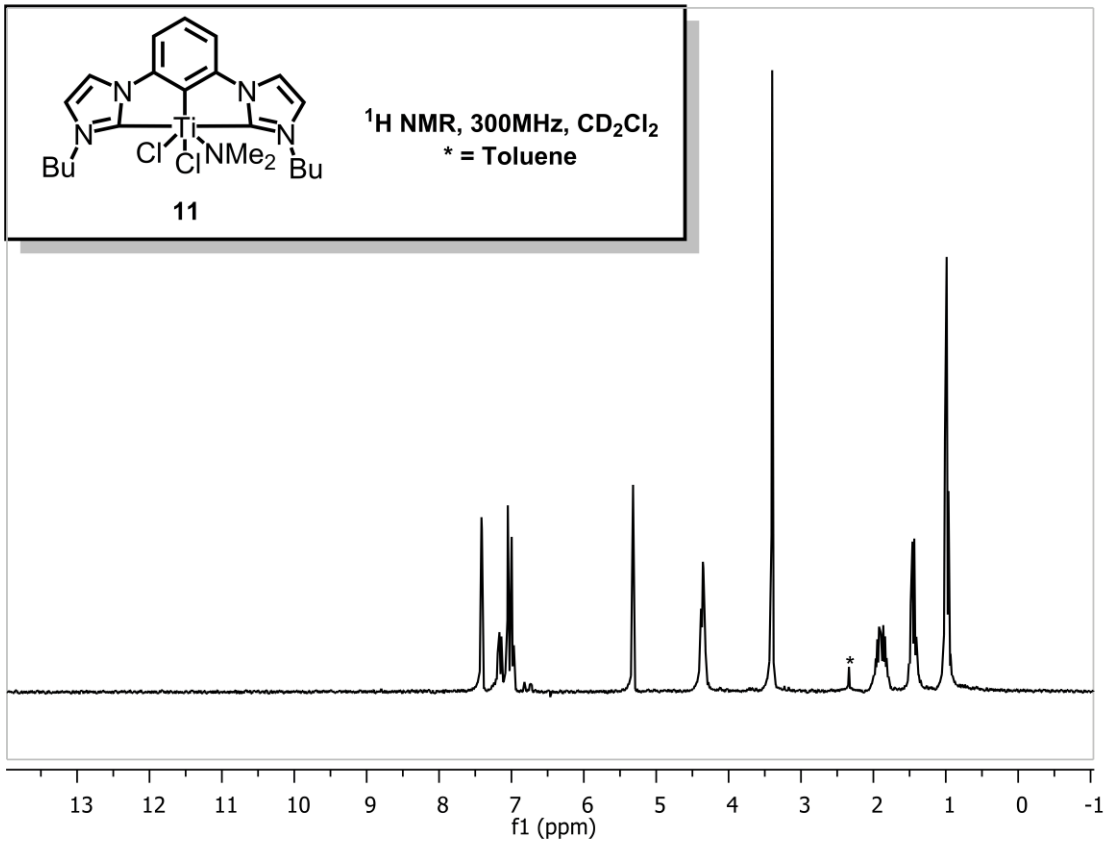
N
Ti
Cl
Cl
Cl
N
N
Bu
8
13C NMR, 500MHz, CD2Cl2
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Bu
N
Cl
Ti
Cl
Cl
Bu
+
9
9'
8
^{1}H NMR, 300MHz, CD_2Cl_2
* = TMSCl
** = N-(trimethylsilyl)dimethylamine
*
**
f1 (ppm)
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1

9
+
9'
+
8
^{1}H NMR, 300MHz, CD_2Cl_2
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
7.05
7.00
f1 (ppm)

9
9'
+
8
** = N-(trimethylsilyl)dimethylamine
* = TMSCl
^{13}C NMR, 300MHz, CD_2Cl_2
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
*
**


9
9'
8
^{1}H NMR, 300MHz, CD_2Cl_2
NMR tube reaction, 104 h
Excess TMSCl
f1 (ppm)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Cl
Cl
NMe2
Bu
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*
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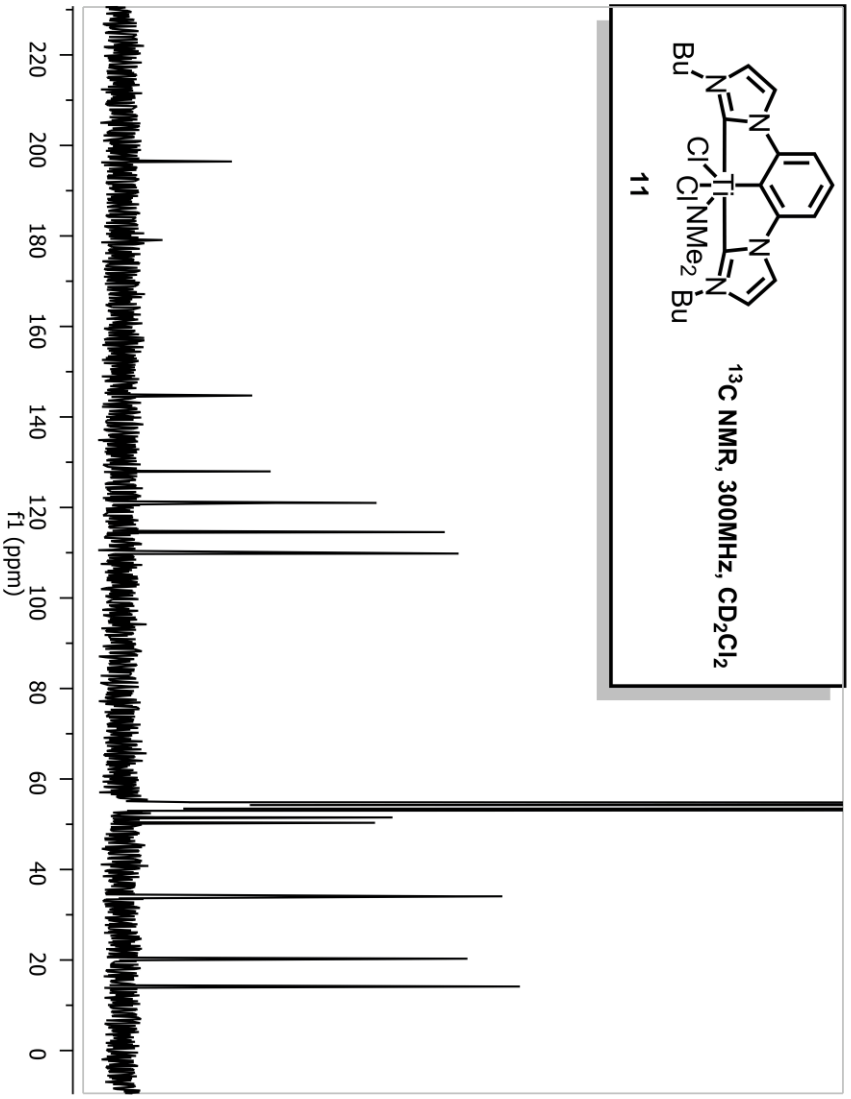
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)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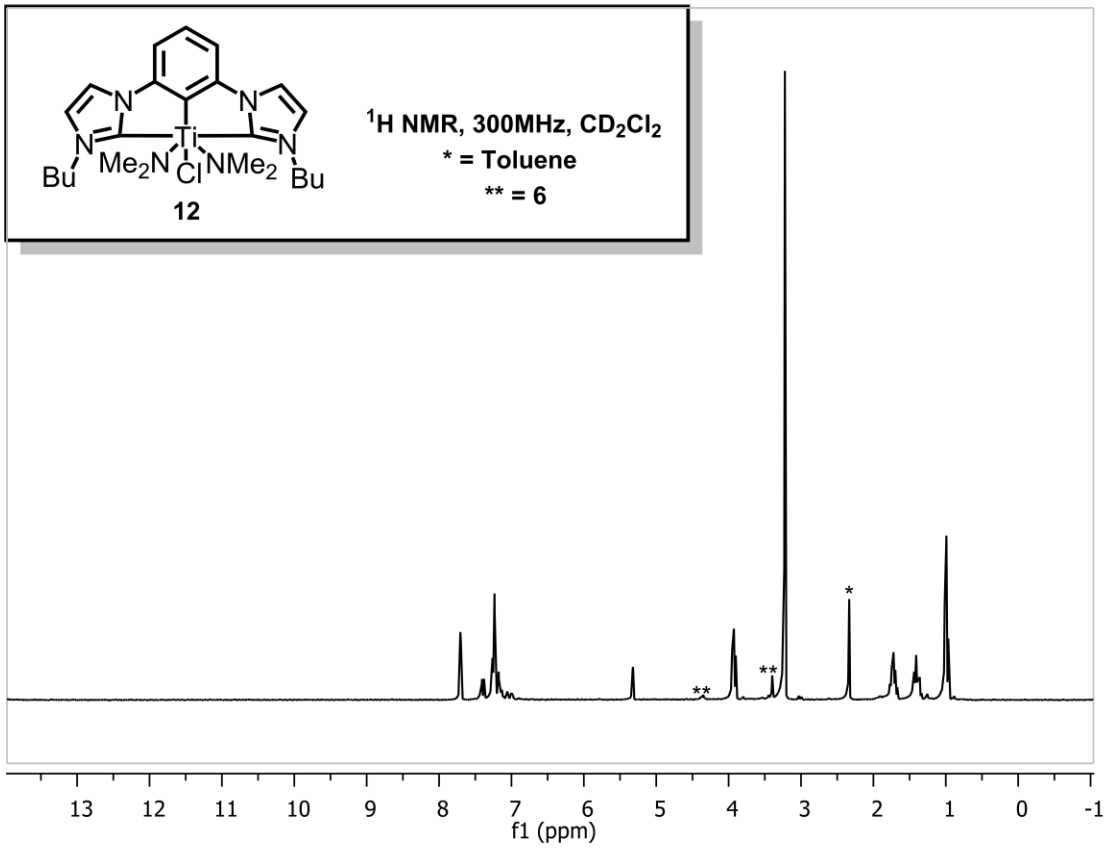
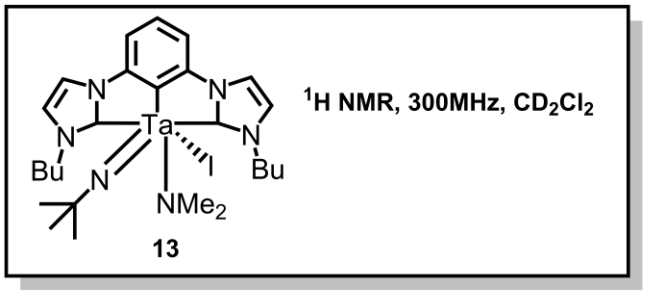
f1 (ppm)
0
20
40
60
80
100
120
140
160
180
200
220

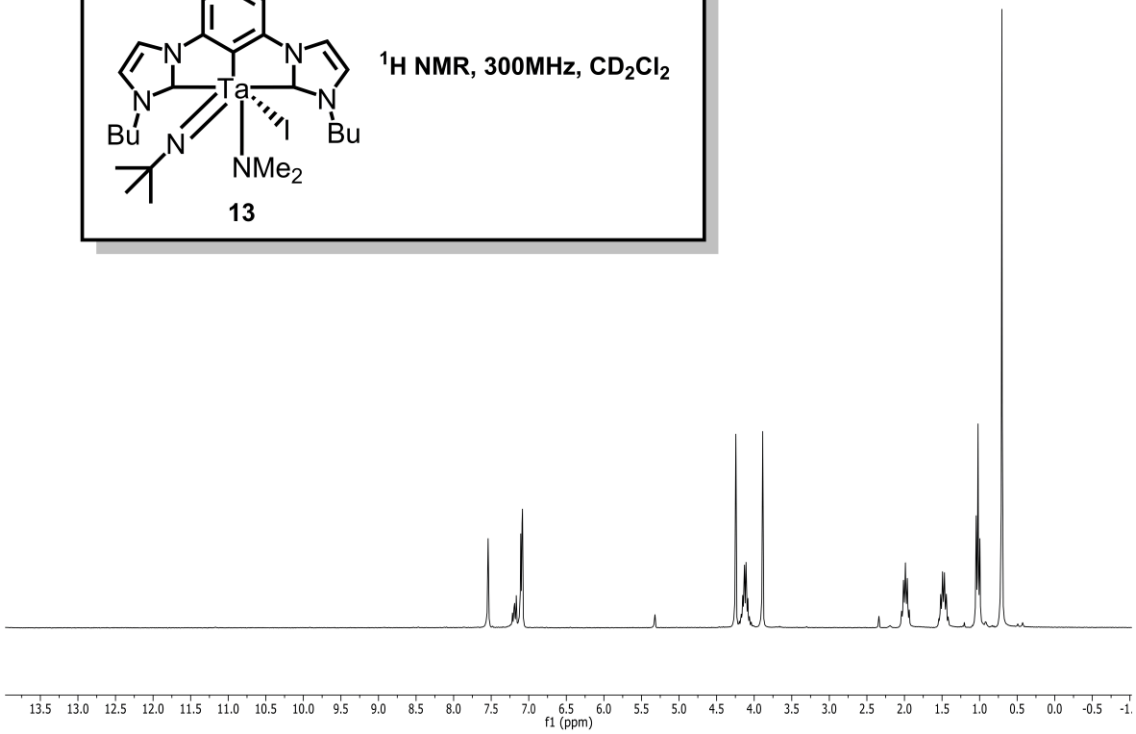

Bu
Me2N
Cl
NMe2
Bu
12
1H NMR, 300MHz, CD2Cl2
* = Toluene
** = 6
*
**
**
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

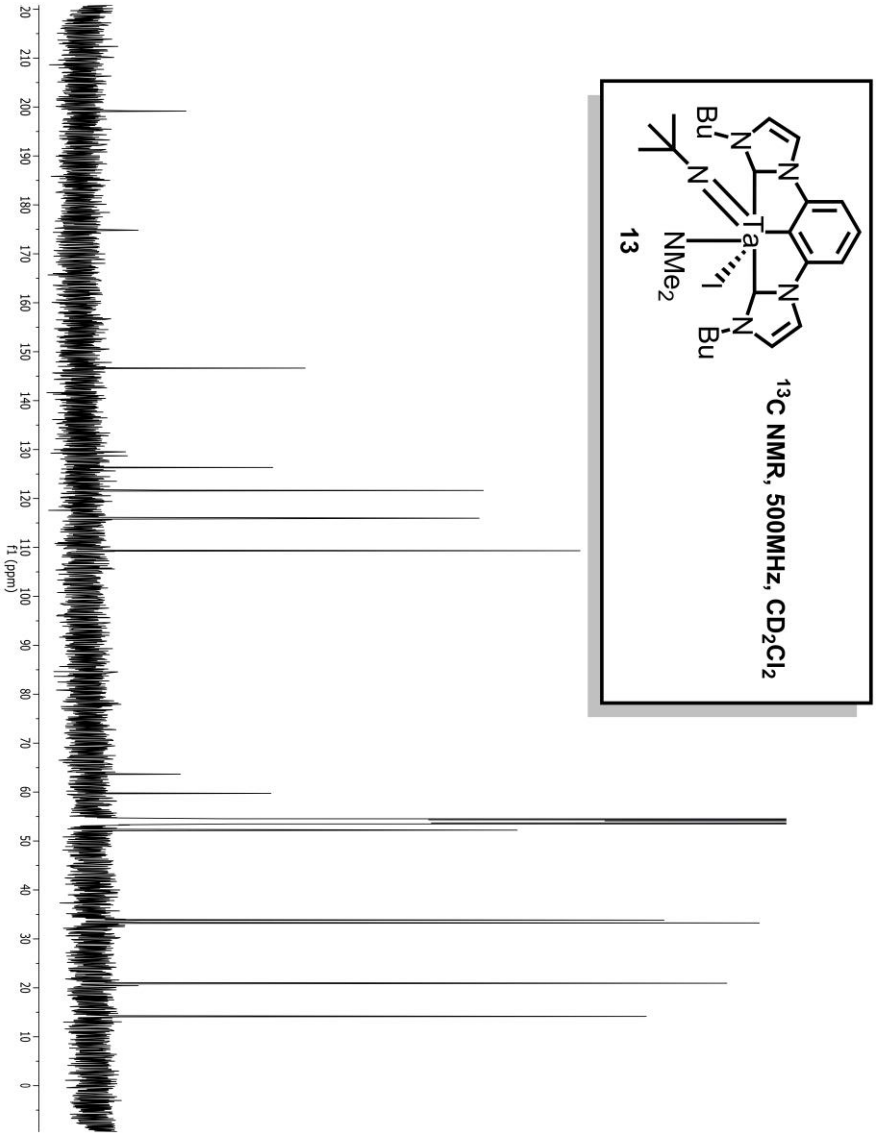
Bu
N
Me2N
Ti
Cl
NMe2
Bu
12
13C NMR, 300MHz, CD2Cl2
* = Toluene
** = 6
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0



13

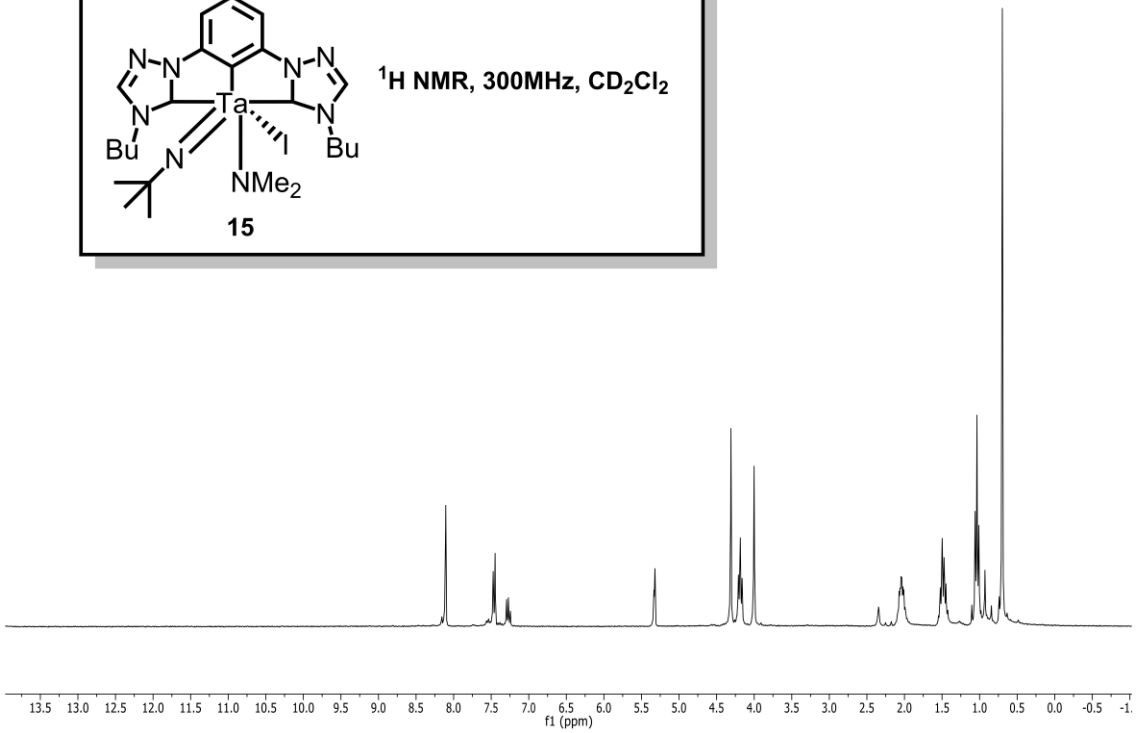
^{1}H NMR, 300MHz, CD_2Cl_2



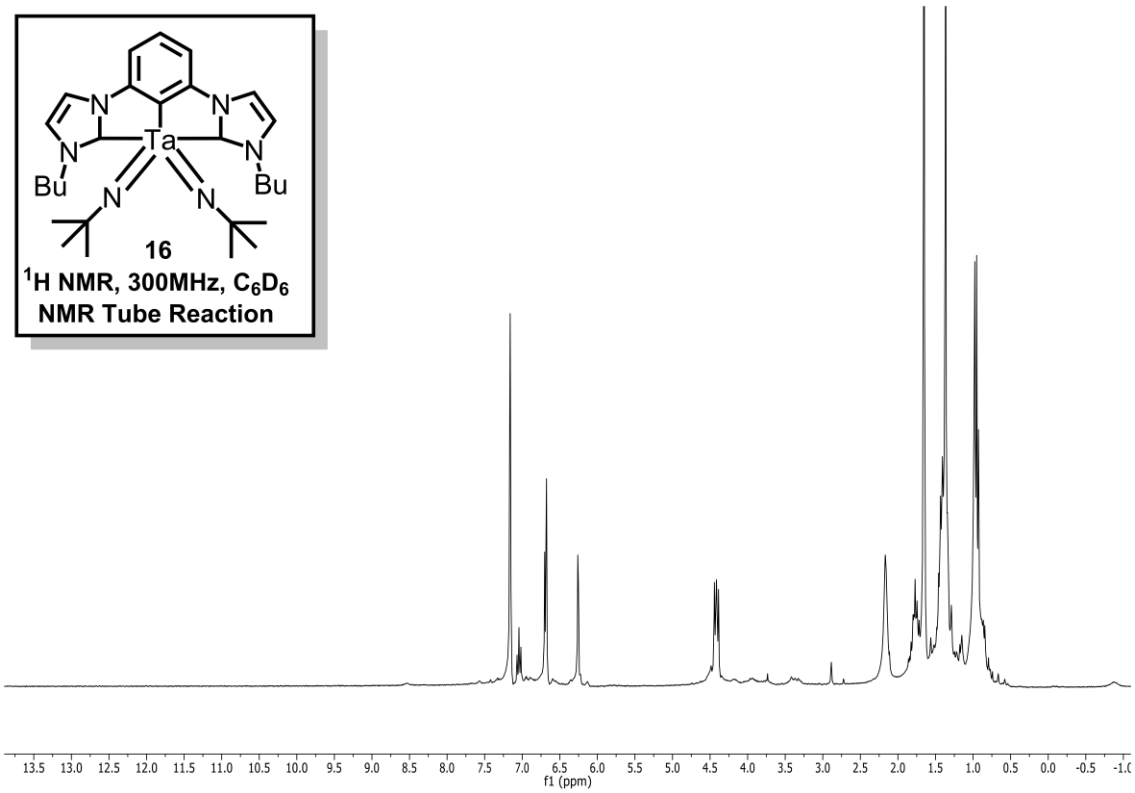

13
^{13}C NMR, 500MHz, CD_2Cl_2
f1 (ppm)

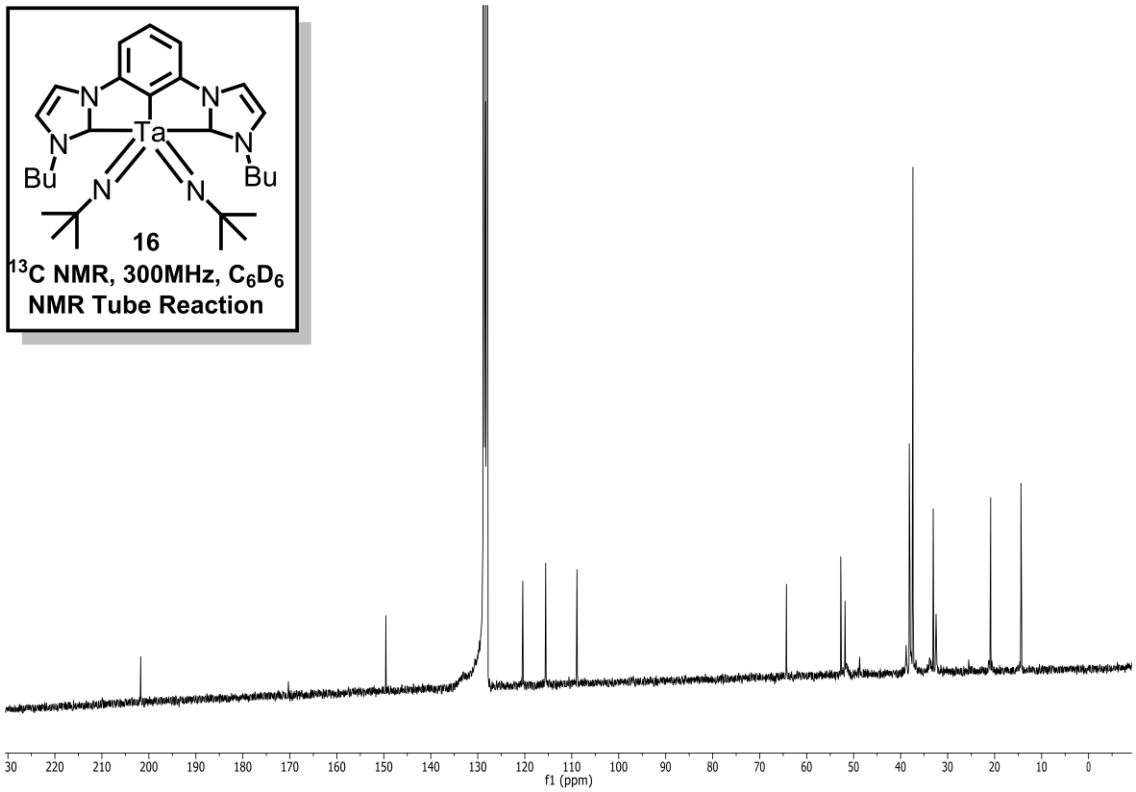
15

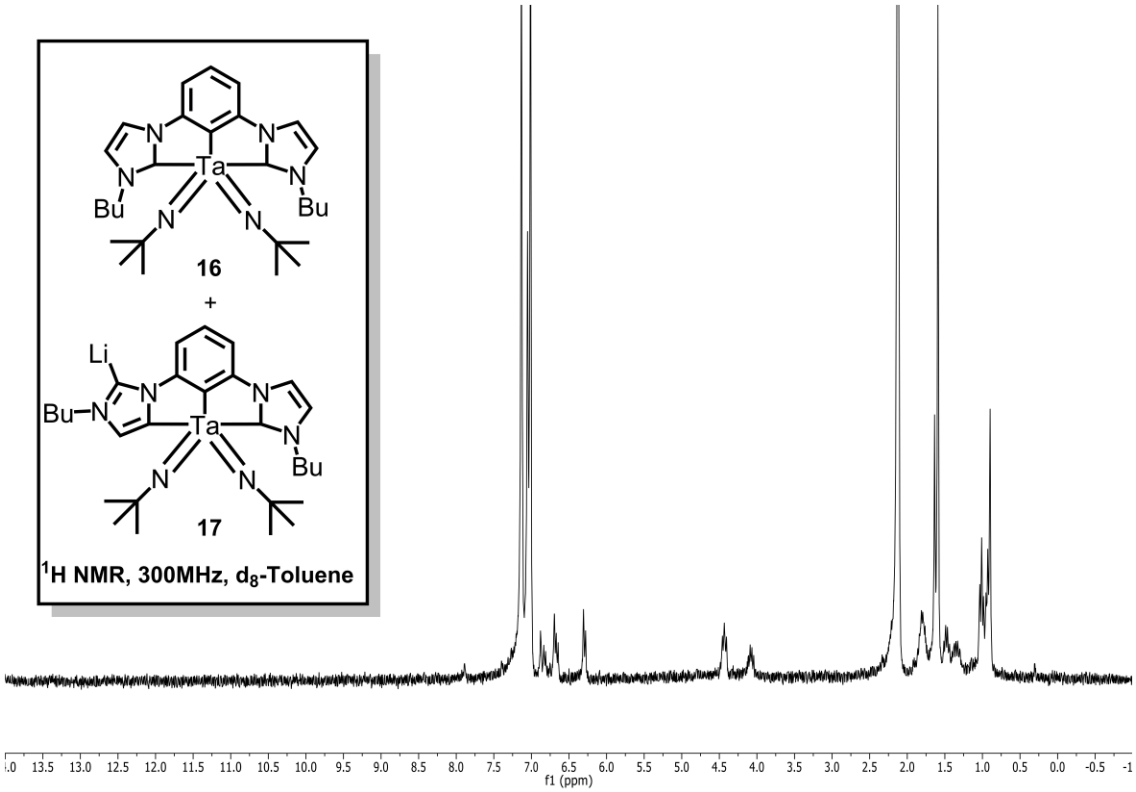
^{1}H NMR, 300MHz, CD_2Cl_2

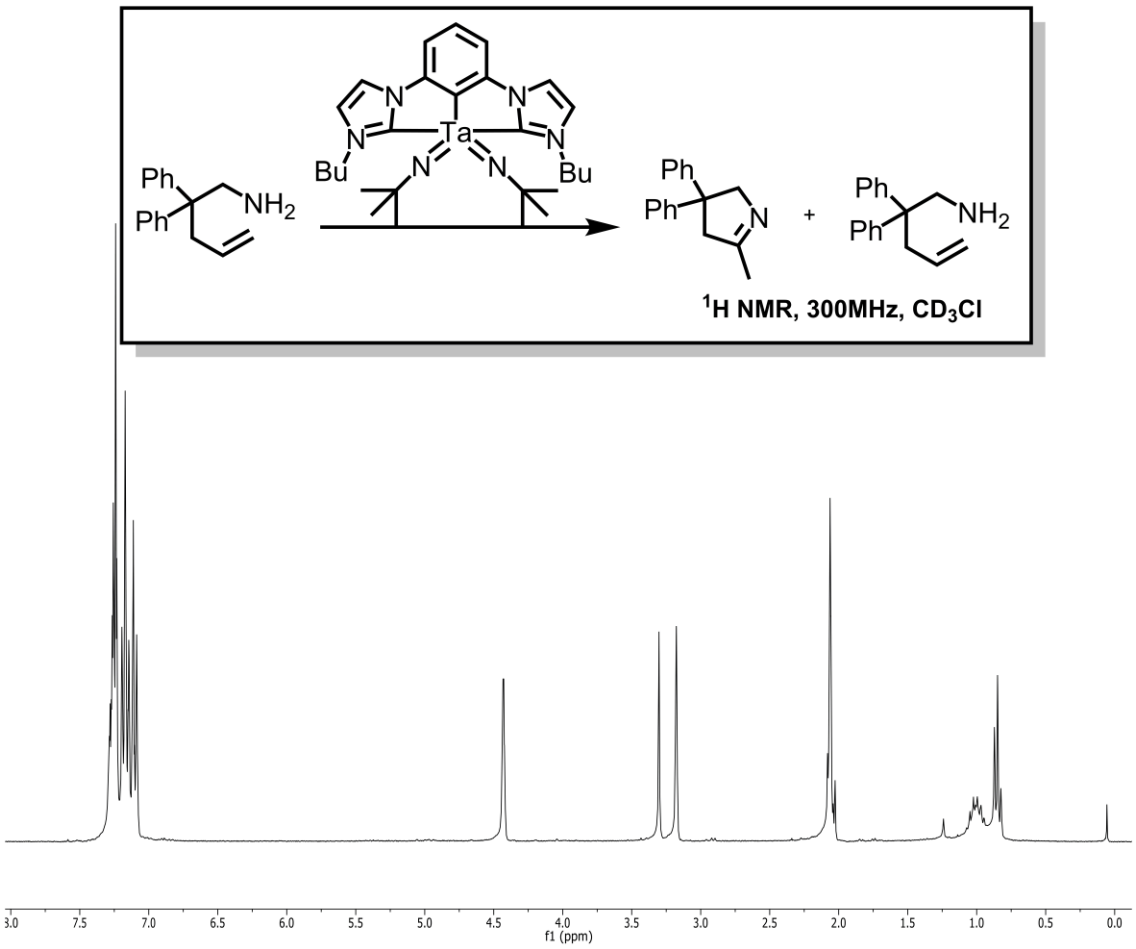


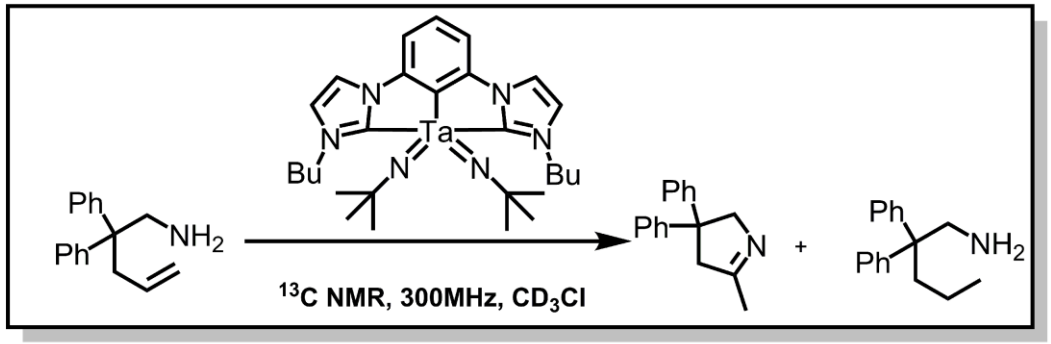
^{13}C NMR, 300MHz, CD_2Cl_2
15
Ta
NMe2
Bu
Bu
f1 (ppm)

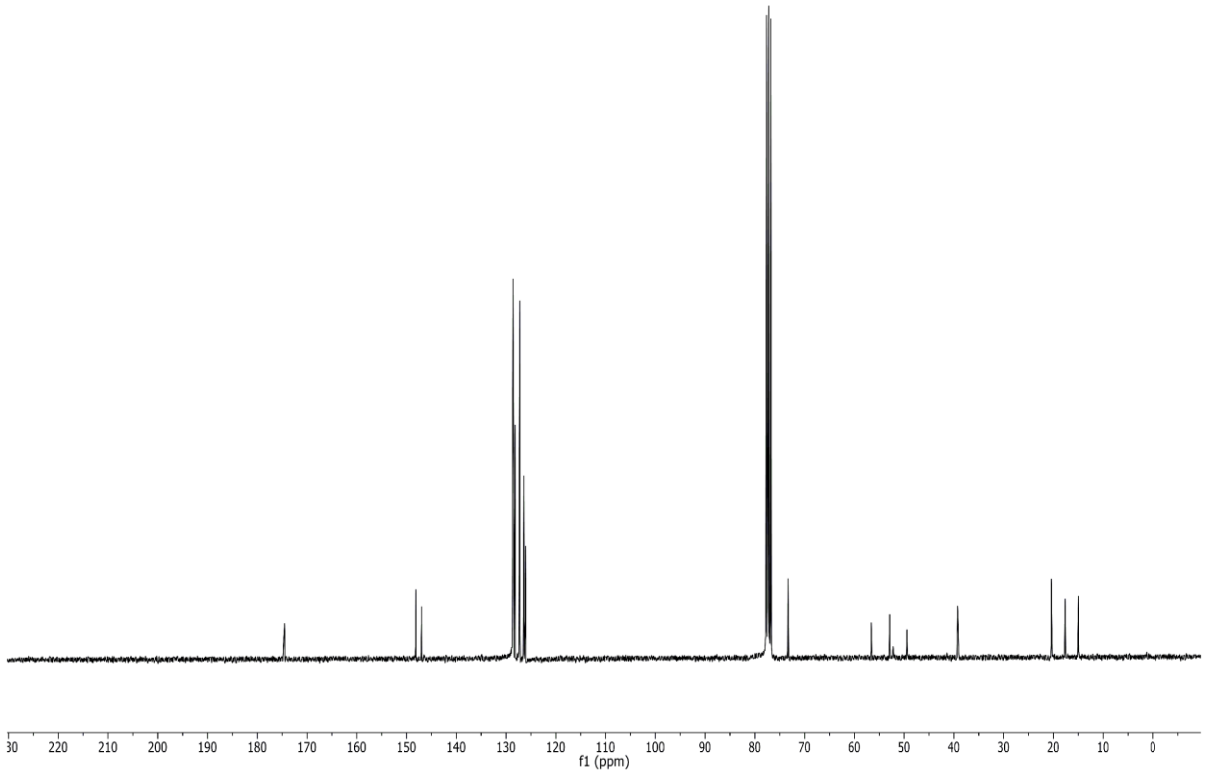

Ta
N
Bu
16
^{1}H NMR, 300MHz, C_6D_6
NMR Tube Reaction
f1 (ppm)

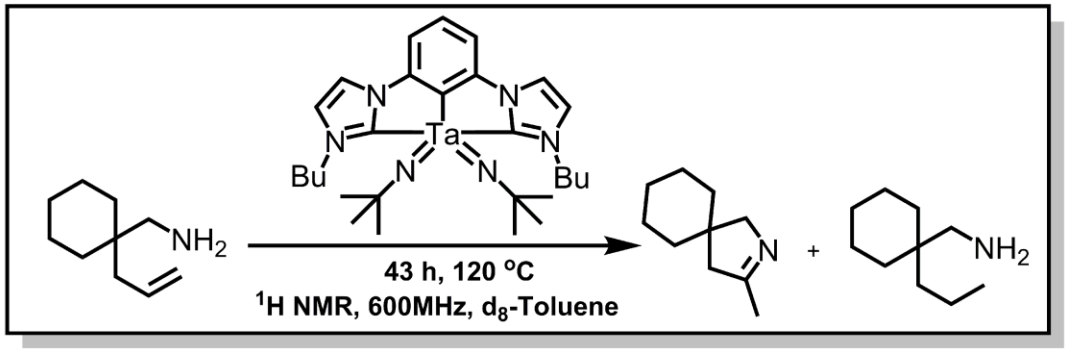

Ta
N
Bu
Bu
16
^{13}C NMR, 300MHz, C_6D_6
NMR Tube Reaction
30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

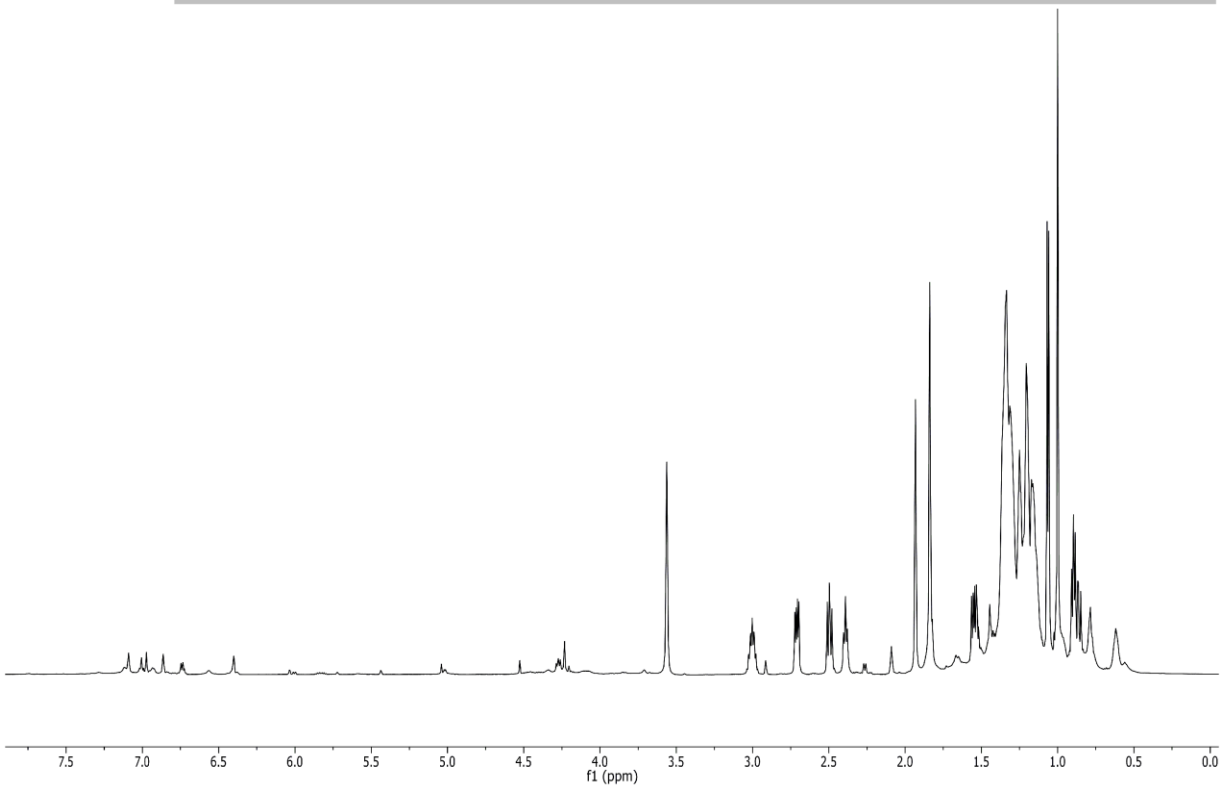

Ta
Bu
Bu
16
+
Li
Bu
Ta
Bu
17
^{1}H NMR, 300MHz, d_8-Toluene
f1 (ppm)

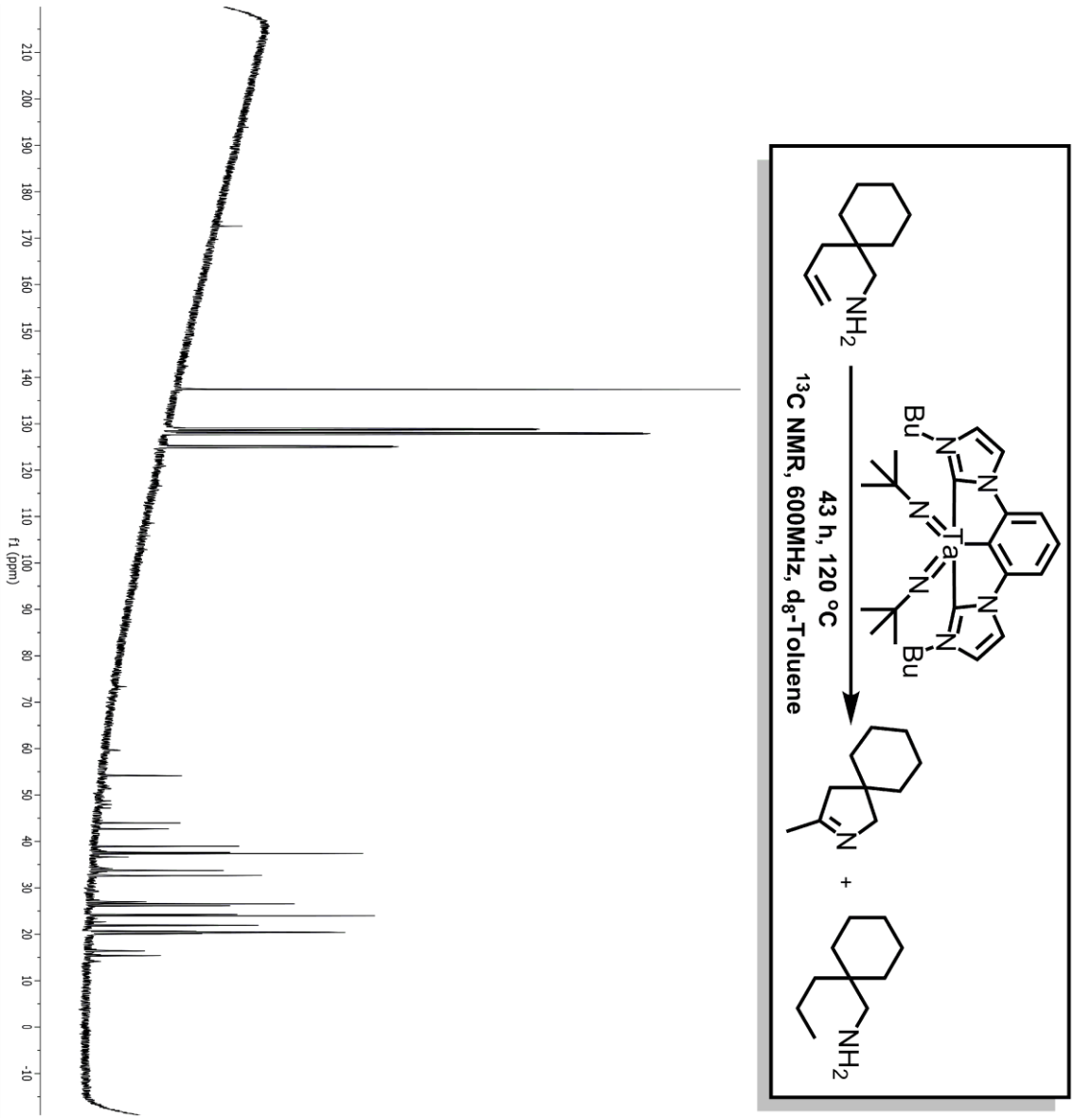

Ph
Ph
NH2
Bu
Ta
N
Bu
Ph
Ph
N
+
Ph
Ph
NH2
1H NMR, 300MHz, CD3Cl
3.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

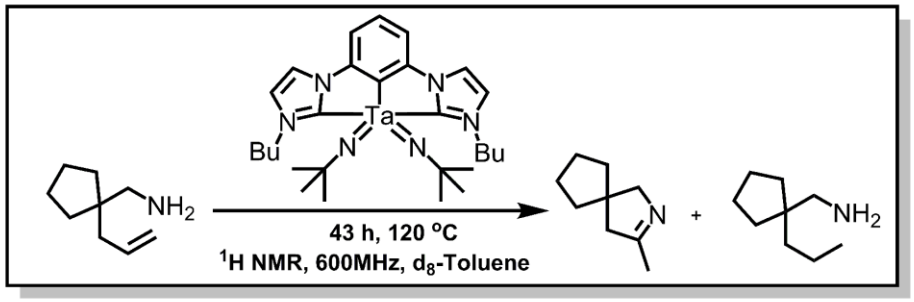

Ph
Ph
NH2
Ta
N
Bu
Bu
Ph
Ph
N
+
Ph
Ph
NH2
13C NMR, 300MHz, CD3Cl

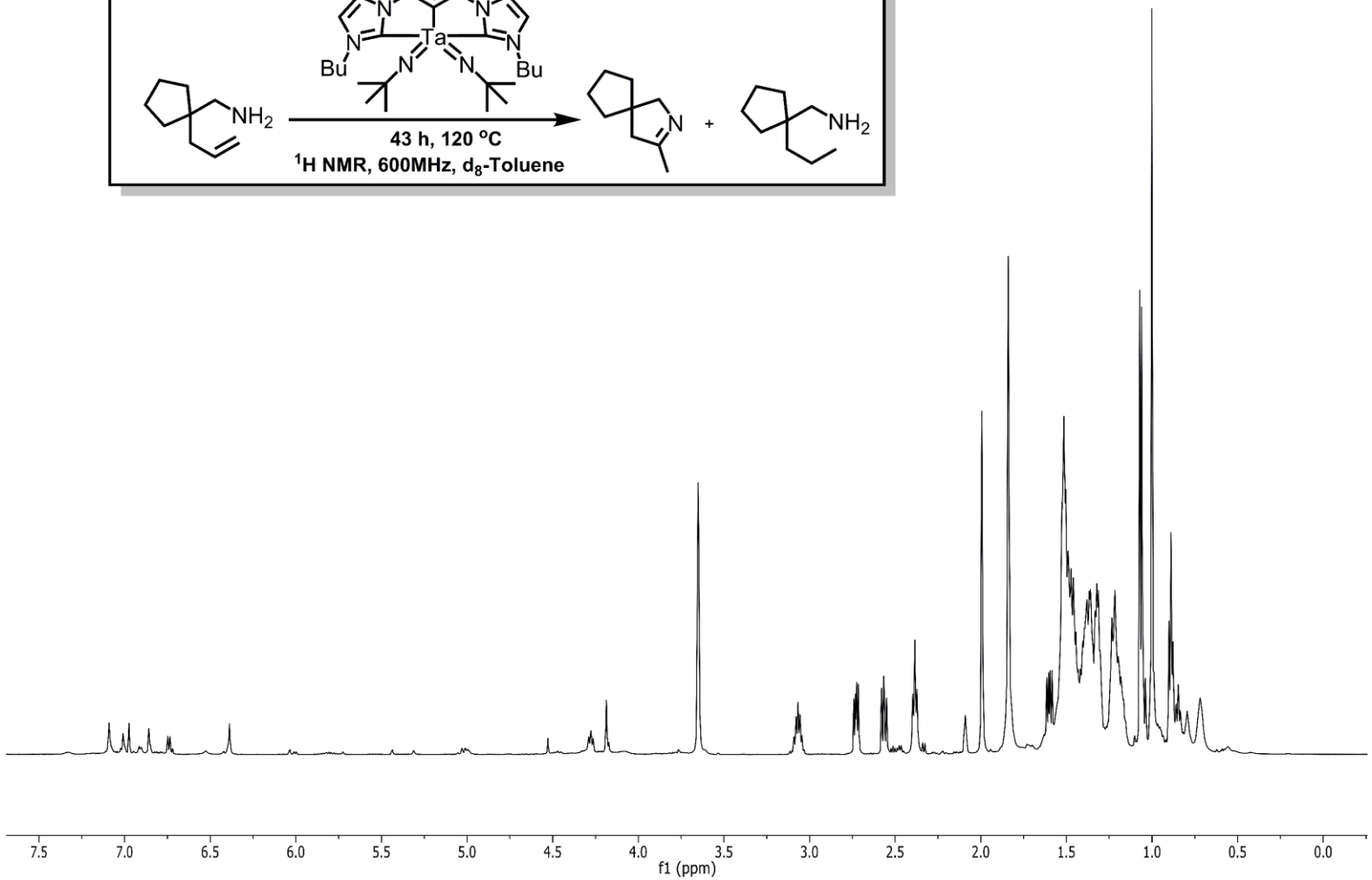

30 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

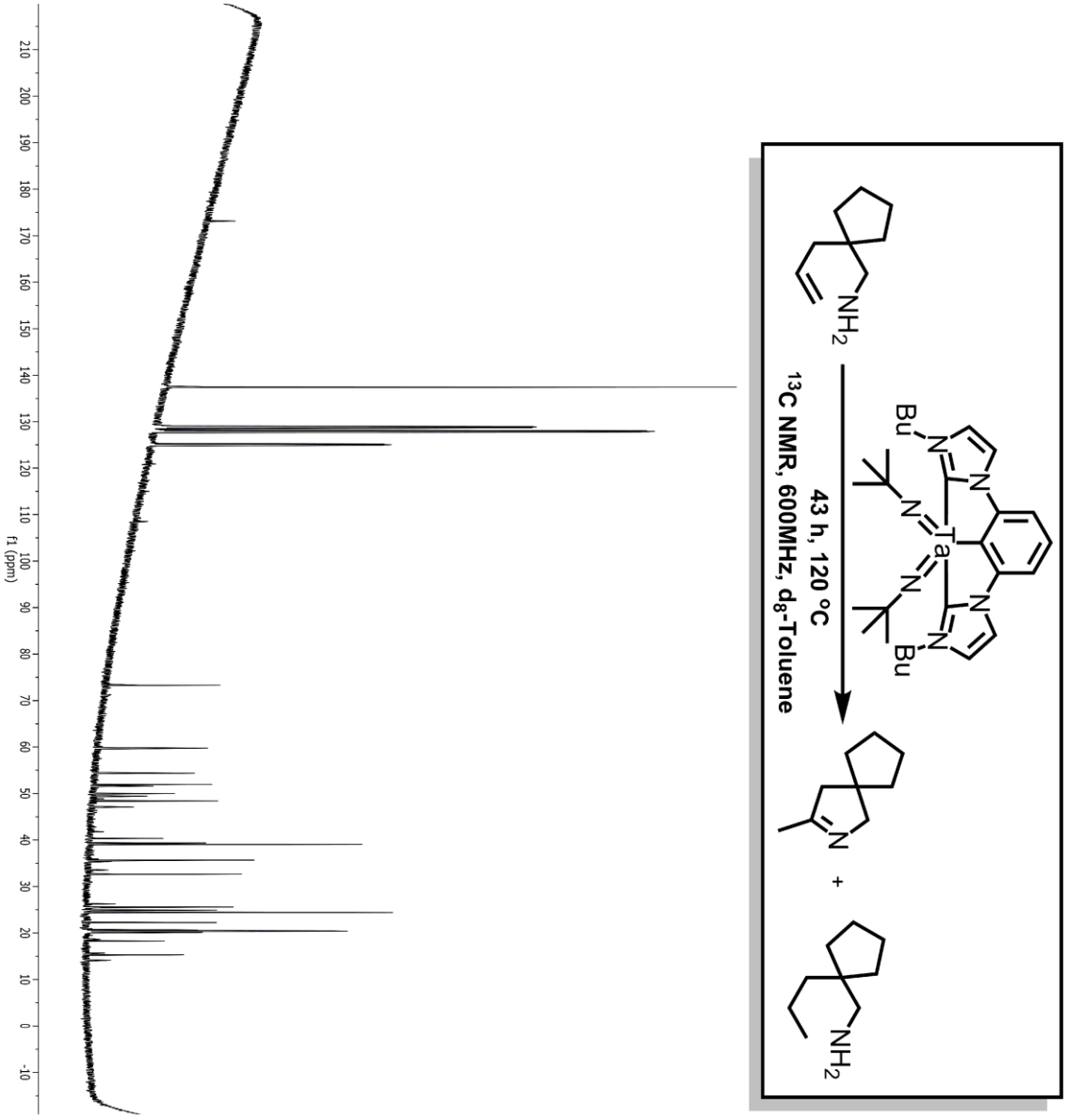

Ta
N
Bu
Bu
NH2
43 h, 120 °C
1H NMR, 600MHz, d8-Toluene
N
+
NH2


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

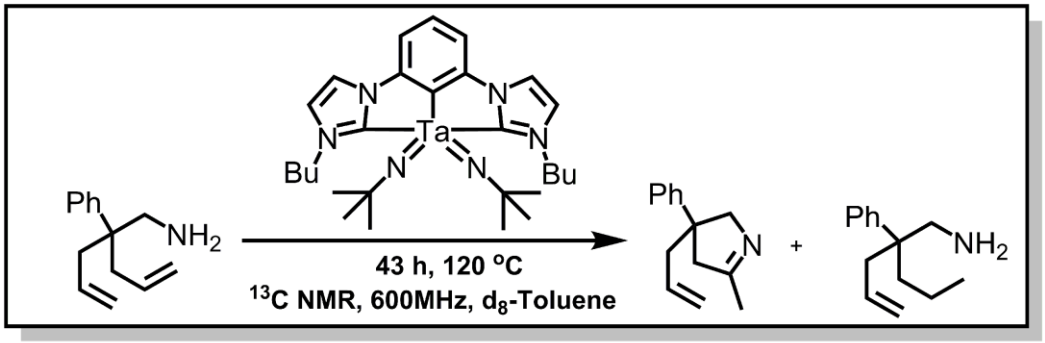

NH2
Bu
N
N
Ta
N
N
Bu
43 h, 120 °C
13C NMR, 600MHz, d8-Toluene
N
+
NH2
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

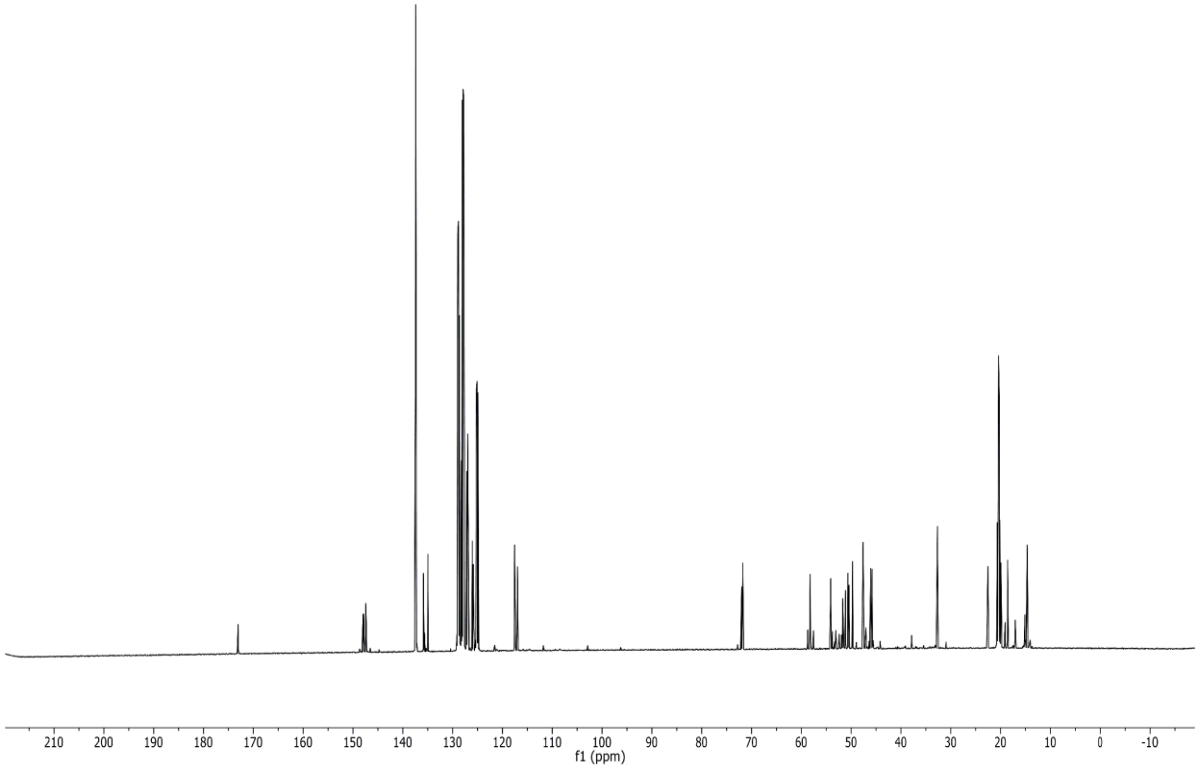

Ta
N
Bu
Bu
NH2
43 h, 120 °C
1H NMR, 600MHz, d8-Toluene
N
+
NH2


7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


NH2
Bu
N
Ta
N
Bu
43 h, 120 °C
13C NMR, 600MHz, d8-Toluene
N
+
NH2
f1 (ppm)

Ph
NH2
Bu
N
N
Ta
N
N
Bu
43 h, 120 °C
1H NMR, 600MHz, d8-Toluene
Ph
N
+
Ph
NH2
f1 (ppm)


Ph
NH2
Ta
N
Bu
Bu
43 h, 120 °C
13C NMR, 600MHz, d8-Toluene
Ph
N
+
Ph
NH2


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

VITA

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